O. Carroll Worley

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PHOTOGRAPHY

ITS PRINCIPLES AND PRACTICE

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FOURTH EDITION—FOURTH PRINTING

WITH CHAPTERS BY
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NEW YORK CITY
D. VAN NOSTRAND COMPANY, INC.
250 FOURTH AVENUE

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TO MY PARENTS

and

A VERY DEAR FRIEND

In the manufacture of this book, the publishers have observed the recommendations of the War Production Board and any variation from previous printings of the same book is the result of this effort to conserve paper and other critical materials as an aid to the war effort.

PREFACE TO THE FOURTH EDITION

For nearly a hundred years photography was largely left to the amateur experimentalist of inadequate technical training who was not able properly to evaluate the results of his experiments from the standpoint of scientific theory. In addition, progress in the science of photography had to wait upon the clarification of certain concepts of the nature of matter and energy. The known facts are now beginning to fit together and order is beginning to appear from among a mass of apparently unrelated phenomena. A true science of photography is emerging.

Moreover, the practice of photography is tending to become more a branch of applied science and less of an empirical craft. It becomes increasingly necessary for practice to be based upon a thorough understanding of photographic materials and processes rather than on rule-of-thumb methods. In a sense, practice has been simplified by advances in the production of more satisfactory new materials and equipment and the development of new and better methods, but the very diversity of these materials and the tremendously increased scope of modern photography combine to demand a more thorough knowledge of fundamentals than was formerly necessary.

Photography is no longer a comparatively simple subject. This is reflected in the present book, which includes many things which were not in the earlier editions, and which assumes a broader background of scientific training than is commonly expected in photographic literature. This is due to the subject matter which does not admit of simple, nontechnical treatment if more than a mere introduction of the subject is intended. The authors have tried to maintain the degree of authority and the point of view that would be expected in a textbook in other branches of science. If this has resulted in some sections being difficult to understand without some technical background, it is but a necessary consequence of the scope of the science and the purpose of the book.

This edition is the work of five authors who have been closely associated as members of the faculty of the Department of Photographic Technology of the Rochester Athenaeum and Mechanics Institute. Each of them has assumed responsibility for separate sections—Color Sensitizing Dyes for Photographic Emulsions is by Ralph H. Braden;

Photographic Optics, Flashlamps and Synchronizers and The Reproduction of Tone are by J. W. Gillon; Photochemistry and the Theory of Development are by Silas M. Thronson and Photography in Colors is by Howard C. Colton. The balance of the book is by the original author.

The rearrangement of the book into sections makes, in the opinion of the authors, for a more orderly and logical presentation of the subject and has facilitated the separation of the sections on the practice of photography from those essentially theoretical. It is hoped that this change will meet with general approval.

References to current literature have been extended. The method used in the last edition whereby references are placed at the bottom of the page on which the subject is mentioned is continued in the present edition. Since there are now a number of journals abstracting photographic literature, no attempt has been made to compile an extensive bibliography. In selecting the references, the following criteria have been employed: (1) the reference provides a good review of the subject as a whole or some special phase of it directly related to the text; (2) the paper is likely to interest the average student; (3) the paper is easy of access and generally in English. The subject index has been made more detailed.

Illustrative examples of commercially available equipment are generally restricted to representative types and the inclusion of any particular piece of equipment does not necessarily imply any preference for it on the part of the authors over similar products of other manufacturers.

The authors are indebted to many for suggestions and asistance and to such an extent that to mention each specifically would extend this preface unduly. The authors trust that those who have had a part in the preparation of this edition will accept this as an acknowledgment of sincere appreciation.

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February 1942
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Rochester, New York

PREFACE TO FIRST EDITION

Manifold as are the applications of photography in all branches of science and industry and great as has been the increase in our knowledge of its basic principles in recent years, comprehensive and adequate instruction in the subject has been largely neglected by our universities and technical institutions. Despite its daily application to the practice of almost every branch of science and industry, and indeed in every walk of life, as well as its importance from the standpoint of pure science, there is not, within the knowledge of the writer, a single university or technical institution in this country which offers a thorough and complete course in the science and practice of photography.

The literature of photography is widely scattered among a large number of journals, some of which have long since disappeared, while until comparatively recently no worthy attempt had been made towards the abstracting and indexing of photographic information. Excluding papers in the periodical press, photographic literature can for the most part be divided into two classes: (1) works of an elementary nature designed for the beginner and paying but scant attention to the fundamental scientific basis of the subject and (2) works of an encyclopedic nature designed principally for reference purposes, such as Dr. J. M. Eder's monumental work in German, the *Ausführliches Handbuch der Photographie* and Fabre's *Traite Encyclopedique de Photographie* in French. Valuable as these works may be, they are not textbooks in the true sense of the word and there is in fact no work dealing both with the science as well as the practice of photography which is especially adapted for use as a test.

The present work is an attempt to meet that need. It embraces the features which several years' experience in the teaching of the subject has shown the writer to be desirable in a work designed for college instruction. No attempt has been made to compile a complete treatise on the subject, while at the same time the fact has been kept in mind that a superficial treatment of the subject, one which is concerned with *effects* rather than causes and with *operations* rather than *scientific principles,* is undesirable in a work of collegiate grade. Accordingly it has been the aim of the writer throughout to present as clearly and as concisely as possible the fundamental principles of the science of photography, omitting nothing of primary importance necessary to an understanding of the subject and paying particular attention to the proper coördination of the facts to one another.

The practical side has not been lost sight of, however, and several of the chapters deal with their subject more from the standpoint of technique rather than science. These, it is hoped, will render the work useful not only to the student but to the practical worker as well.

An apology, perhaps, is due for the omission of certain subjects and for the brief treatment accorded to others. This was, however, to a certain extent, demanded by the scope of the work which is that of a text rather than a treatise. Accordingly a large number of the unsettled controversies have either been omitted, or but briefly treated, as it was felt inadvisable to consider in a work of this nature subjects which still await satisfactory solution.

Footnotes throughout the text will show the extent to which I am indebted to others, while to the following authorities I desire to place on record my appreciation of their invaluable services: Dr. C. E. K. Mees, Dr. S. E. Sheppard, Dr. A. P. H. Trivelli, all of the Eastman Research Laboratory; Mr. F. F. Renwick; Dr. Walter Clark of the British Photographic Research Association; Dr. Hermann Kellner of the Scientific Department, Bausch and Lomb Optical Company; Carl J. Reich of the Gundlach-Manhattan Optical Company; Mr. George E. Brown, Editor of the *British Journal of Photography*; Mr. Frank Roy Fraprie and Mr. E. J. Wall of *American Photography*; Drs. Walters and Davis of the Bureau of Standards; and Miss Bess Spence of this institution who has assisted me in seeing the work through the press. To all others who have assisted in the preparation of this work in any way, a cordial acknowledgment of appreciation is also due.

C. B. NEBLETTE

COLLEGE STATION, TEXAS, 1920

ABBREVIATIONS FOR JOURNALS

Amateur Photographer. Amat. Phot.
American Photography. Amer. Phot.
American Cinematographer. Amer. Cinemat.
Annales de Physique. Ann. d Phys.
Astrophysical Journal. Astrophysical J.
British Journal of Photography. Brit. J. Phot.
British Patent. B.P.
Bulletin, American Physics Society. Bull. Amer. Phys. Soc.
Bulletin de la Société française de Photographie. Bull. Soc. franç. Phot.
Bureau of Standards Journal of Research. Bur. Stand. J. Res.
Camera (Luzern). Camera (Luzern)
Camera (Philadelphia). Camera (Phila.)
Camera Craft. Camera Craft.
Chemical Abstracts (American Chemical Society). Chem. Abst.
Chemie et Industrie. Chem. et Ind.
Commercial Photographer. Commercial Phot.
Comptes rendus. Compt. rend.
Das Atelier des Photographen. Das Atelier
Eder's Jahrbuch für Photographie. Eder's Jahrbuch
French Patent. F.P.
German Patent. D.R.P.
Journal of the American Chemical Society. J. Amer. Chem. Soc.
Journal of Applied Physics. J. Applied Phys.
Journal of Chemical Education. J. Chem. Ed.
Journal of Industrial and Engineering Chemistry. J. Ind. & Eng. Chem.
Journal of the Chemical Society (London). J. Chem. Soc.
Journal of the Franklin Institute. J. Franklin. Inst.
Journal of the Optical Society of America. J. Opt. Soc. Amer.
Journal of the Photographic Society of America. J. Phot. Soc. Amer.
Journal of Physical Chemistry. J. Phys. Chem.
Journal of the Society of Chemical Industry (Gt. Britain). J. Soc. Chem. Ind.
Journal für Praktische Chimie. J. für Prak. Chim.
Journal of the Society of Motion Picture Engineers. J. Soc. Mot. Pict. Eng.
Kinotechnik. Kinotechnik
Klimsch's Jahrbuch. Klimsch. Jahr.
National Lithographer. Nat. Lith.
Nature. Nature
Philosophical Magazine. Phil. Mag.
Photographic Journal. Phot. J.
Photographische Chronik. Phot. Chron.
Photographische Industrie. Phot. Ind.
Photographische Korrespondenz. Phot. Korr.

Photographische Mitteilungen. Phot. Mitt.
Photographische Rundschau. Phot. Rund.
Photographische Wochenschrift. Phot. Woch.
Photo Engraver's Bulletin. Photo Engraver's Bull.
Photo Technique. Phot. Tech.
Physical Review. Phys. Review
Popular Photography. Popular Phot.
Proceedings of the Royal Society. Proc. Royal Society
Professional Photographer. Professional Phot.
Revue française de Photographie. Rev. franç. Phot.
Science et Industries Photographiques. Sci. et Ind. Phot.
Transactions of the Faraday Society. Trans. Farad. Soc.
Transactions of the Illuminating Engineering Society. Trans. Ill. Eng. Soc.
Transactions of the Royal Society of Edinburgh. Trans. Royal Soc. Edinburgh.
Transactions of the Society of Motion Picture Engineers. Trans. Soc. Mot. Pict. Eng.
United States Patent. U.S.P.
Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie. Z. wiss. Phot.
Zeitschrift für Physik. Z. Physik.
Zeitschrift für Elektrochemistrie. Z. Elektrochem.

CONTENTS

CHAPTER PAGE

SECTION 1. THE HISTORY OF PHOTOGRAPHY

1. The History of Photography 1

SECTION 2. THE OPTICS OF PHOTOGRAPHY

2. Photographic Optics 48
3. The Photographic Objective 90
4. The Camera and Accessories 124
5. Light Sources for Photography 167

SECTION 3. THE THEORY OF THE PHOTOGRAPHIC PROCESS

6. Introduction to Photochemistry 206
7. The Photographic Emulsion 230
8. Color Sensitizing Dyes for Photographic Emulsions 249
9. The Latent Photographic Image and its Development .. 290
10. Developing Agents and Solutions 315
11. Fixing, Washing and Drying 352
12. The Structure of the Photographic Image 373

SECTION 4. PHOTOGRAPHIC SENSITOMETRY AND THE REPRODUCTION OF TONE

13. Photographic Sensitometry 390
14. The Reproduction of Tone 440
15. The Reproduction of Color in Monochrome 456

SECTION 5. NEGATIVE PROCESSES

16. Negative Materials 475
17. Exposure of the Negative 503
18. Negative Development 518
19. Defects in Negatives 556
20. Intensification and Reduction of the Negative 565
21. After Work on the Negative 582

SECTION 6. POSITIVE PROCESSES

22. Developing-out Papers 592
23. Contact and Projection Printing 616

CHAPTER PAGE
24. Toning of Developed Silver Images 644
25. Bichromated-Colloid Processes 662
26. Platinum, Palladium, Iron and Plan-copying Processes 692
27. Finishing and Mounting the Print 705
28. Lantern Slides and Transparencies 718

Section 7. Photography in Color

29. Principles of Three-Color Photography 733
30. Three-Color Negative Making 745
31. Subtractive Paper Printing Processes 762
32. Screen and Lenticular Processes 784
33. Integral Tripacks 801
34. Accuracy of Color Reproduction 815

CHAPTER I

THE HISTORY OF PHOTOGRAPHY

Introduction.—Photography, from the Greek meaning to draw with light, is the science of obtaining images of objects by the action of light on sensitive substances. It is not definitely known to whom the word itself is due. The first use of the word is generally accredited to Sir John Herschel in a paper before the Royal Society, March 14, 1839. The German historian of photography, Eric Stenger, however, has established the fact that the word appeared in a newspaper account of the work of Fox-Talbot, published in the Vossische Zeitung, February 25th of the same year.[1]

The Camera Obscura.[2]—No one knows when the formation of an image by the light admitted through a small opening was first observed. The first reliable recorded observation of this simple and fairly common phenomena appears in the *Problemata* of Aristotle, published about 350 B.C. There are other references in the works of Roger Bacon (1214–1292) and the *Thesaurus Opticae* of Alhazen published about 1100, but these are rather vague. Leonardo da Vinci, in one of his manuscripts, shows a diagram with the arrangement of the aperture, the screen and the course of the light rays. This manuscript, however, was not published until 1797.

The camera obscura was apparently well known in the early 16th Century in both Italy and in Germany, as numerous references have been found.[3]

The *Magia Naturalis* of Jean Baptiste Porta, which appeared at Naples in 1553, did so much to make the camera obscura known, that its author was for a long time credited with its discovery. This we now know to be incorrect, as there are at least five unmistakable references to the camera obscura in books published before his *Magia Naturalis*. This work, unlike those which had preceeded it, was a

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[1] Stenger, *Brit. J. Phot.* **79** (1932) 578.

[2] Camera Obscura—from the Latin *camera* room and *obscura* dark.

[3] Cardan, *De Subtilitate* (Nuremberg 1550). Frisius, *De Astronomics et Geometrics* (1545).

Barclay—Origin of the Word Photography. Phot J. **77** (1937) 528.

popular rather than a scholarly work, and consequently reached a larger audience.

The earliest recorded description of a camera with a lens appears to be that in a book on perspective *La Practica della Perspectiva* by a Venetian nobleman, Daniello Barbaro, published in 1568. Another description of a camera obscura with lens is found in a work by Benedetti of Venice published in 1584, and finally Kepler in his *Dioptrice,* published in 1611, dealt with the optics of the camera obscura at length, pointing out the advantages of a compound lens over the simple plano-convex lens used by Barbaro.[4]

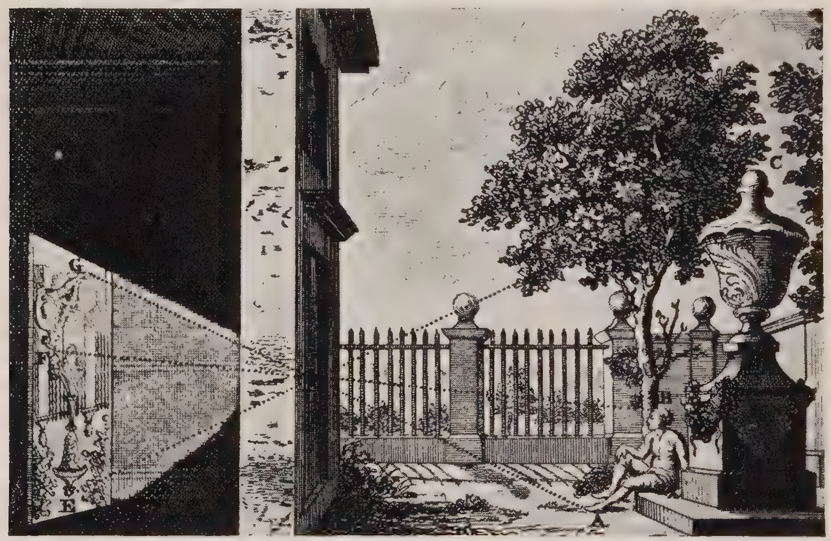

FIG. 1. The Camera Obscura From an Old Print. (Courtesy of the Smithsonian Institution.)

After the middle of the 18th Century, the camera obscura became well known as an instrument for sketching or for amusement at the seaside and other resorts. Several types designed for these purposes are described and illustrated, for example, in a *Treatise on Optics* by Joseph Harris, published in London in 1775 and in Gravesandeo, *Perspective,* published in London 1724.[5]

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[4] Other references to the optics of the camera: Edition of Euclid's *Optics* by Dante (Florence 1573). Risner, *Opticae* (Cassel 1606).

[5] See: Von Rohr and Court, *Phot. J.* **75** (1935) 54.

WATERHOUSE—History of the Camera Obscura. Phot. J. **40** (1900) 270.

Early Photochemistry.—Since in general photography is concerned with light-sensitive compounds of silver, we may pass over those observations of the alchemists of the middle ages on the alteration of other substances upon exposure to light or the atmosphere. The first observations of the sensitivity of silver salts, recorded by Pliny in the first century, are only a record of the action of the atmosphere on metallic silver. In the eighth century Geber observed the darkening of silver nitrate, and Georgius Fabricus, in 1556, the darkening of horn silver, a crude form of silver chloride found in the mines of Frieburg; which both attributed to the action of vapors in the atmosphere. That the darkening of silver salts, and particularly silver chloride, is due to light and not to the action of various vapors of the atmosphere was definitely recorded by Johann Heinrich Schulze in 1727, a member of the faculty of the University of Altdorf, where, as a typical man of science of his day, he taught a number of subjects, including anatomy, botany, geography and philology. Schulze coated

Fig. 2. Johann Heinrich Schulze. (From Eder, *Ausführliches Handbuch der Photographie.*)

paper with a solution of silver chloride and by exposing it to light made copies of stencils cut in black paper.[6] For this achievement, he has been termed the discoverer of photography, but this is unfair to others as he did not attempt to use the camera obscura nor was he successful in finding a means of rendering the image permanent. When exposed to light it rapidly darkened all over.

FIG. 3. Thomas Wedgwood from a Chalk Drawing. Author Unknown.

Carl Wilhem Scheele, the great Swedish chemist, investigating the chemical changes involved in the darkening of silver chloride, discovered that the material was decomposed to silver with loss of chlorine. He also noted the difference in the rates of darkening obtained with light of different colors. Scheele, remarks Dr. S. E. Sheppard,[7] should be regarded as the founder of the photochemistry of the silver salts. The closing years of the eighteenth and the nineteenth century witnessed a large number of observations on the action of light on various substances, but as these played no part in the invention of photography they may be passed over.

The Beginning of Photography—Wedgwood and Davy. —The first definite step towards the discovery of photography was made by Thomas Wedgwood, fourth son of the great English potter, at the turn of the century. Wedgwood, together with Humphrey Davy, then a rising young chemist, repeated the work of Schulze with silver nitrate. They were able to make prints of leaves

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[6] A translation of Schulze's paper appeared in *Phot. J.* **38** (1898) 53. For readers of German, there is an interesting biography of Schulze by Eder, *Johann Heinrich Schulze* (Wien 1920).

[7] *J. Chem. Ed.* **4** (1927) 300.

WATERHOUSE—The Development of Photography with Salts of Silver. Phot. J. **43** (1903) 159.

and similar objects, but were unable to prepare a paper sufficiently rapid to permit its use in the camera obscura. Davy made some important additions to the work of Schulze. He found that silver chloride was more sensitive than silver nitrate, and that by using the concentrated light of a solar microscope, he was able to secure images of small stationary objects. But neither Wedgwood nor Davy was able to find a means of "fixing" the image or dissolving the unacted-upon silver salt so as to render the image permanent. The poor health of Wedgwood was no doubt partly responsible for this, and the whole subject was abruptly terminated by his death at the early age of thirty-one years. After his death, a joint paper, written probably by Davy, was brought before the Royal Institution and appeared in the Journal for 1802 under the following title: *An Account of a Method of Copying Paintings Upon Glass, and of Making Profiles by the Agency of Light on Nitrate of Silver,* by T. Wedgwood, with observations by H. Davy.

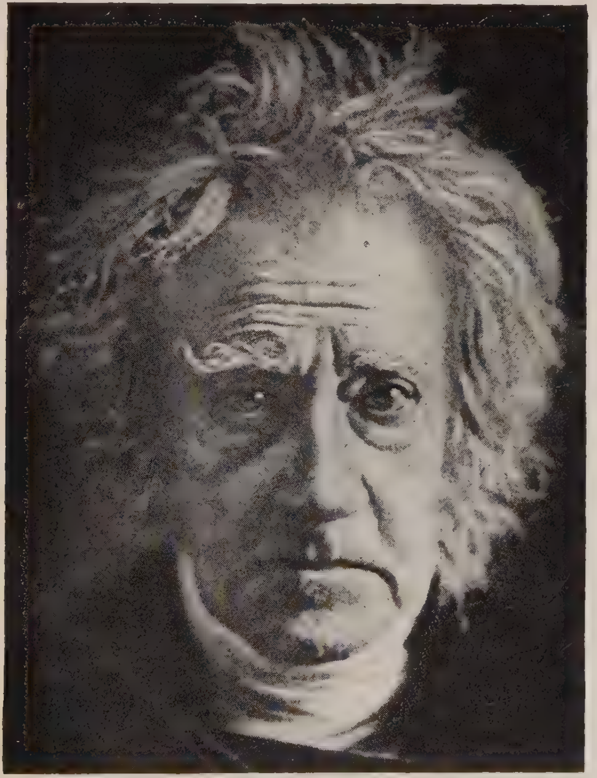

Fig. 4. John Herschel. From a Photograph by Mrs. Julia Cameron.

Discovery of a Fixing Agent.—Herschel in 1819 discovered the solubility of the silver halides in sodium thiosulfate which he termed *hyposulfite,* hence the name hypo. Thus was made available the fixing agent which Wedgwood and Davy had sought in vain. So little attention, however, did this paper receive, that it appears to have been unknown to Talbot, Niepce or Daguerre, and it was only after Herschel had called attention to its use as a fixing agent, following the publication of the investigations of Talbot early in 1839, that it replaced sodium chloride (salt) for this purpose.

Niepce.—The first to produce a permanent image was Joseph Nicephore Niepce, born at Chalon-sur-Saône, France, in 1765 and died in 1833.[8] Unfortunately Niepce left no written account of his work and our only source of information is his correspondence with his brother Claude who lived in London during most of the time Nicephore was occupied with these investigations. We know that he

Fig. 5. Nicephore Niepce. (Courtesy Société française de la Photographie.)

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[8] For an interesting account of Niepce see: Fouque, *The Truth on the Invention of Photography.* Translated by Epstean (New York 1935).

became very much interested in the process of lithography, and in 1813 experimented with silver chloride in an effort to copy designs on the stone so as to save lithographers the labor of transferring the drawing by hand. We know, from a letter to his brother Claude, that he was successful in securing a negative image in the camera as early as 1816. In a letter dated May 5, 1818, we find him writing:

"When my object-glass was broken, no longer being able to make use of my camera, I made an artificial eye with Isidore's ring box, a little thing from 16 to 18 lines square. I had, luckily, the lenses of the solar microscope, which, as you know, belonged to our grandfather Barrault. One of these little lenses proved to be exactly of the focus wanted; and threw a picture of objects in a very sharp and life-like manner on to a field of thirteen lines diameter.

"I placed this little apparatus in my workroom facing the open window looking on to the pigeon-house. I made the experiment in the way you are acquainted with, my dear friend, and I saw on the white paper the whole of the pigeon-house seen from the window, and a faint impression of the window frame itself which was not exposed to the sunlight. One could distinguish the effects of the solar rays in the picture from the pigeon-house up to the window-sash. This is but a very imperfect experiment, but the images of the objects were extremely minute. The possibility of painting by this means appears almost clear to me; and if I am able to perfect my process, I shall hasten to respond to the interest which I know you will take in it, by imparting it to you. I do not hide from myself that there are great difficulties, especially as regards fixing the colours, but with work and patience one can accomplish much. What you had foreseen has proved true. The ground of the picture is black, and the objects are white, that is to say lighter than the ground."

This was the first camera negative. Apparently, he was unable to find a fixing agent which would remove the unaltered silver halide and render the image permanent, for later we find him turning to bitumen.

Metal plates coated with a layer of bitumen were exposed beneath the transparent tracing to be reproduced, then bathed in oil of lavender which removed the bitumen from the unexposed portions of the plate leaving bare the metal base. These portions were then etched in an acid bath, the bitumen remaining in the exposed portions acting as a resist; thus producing an image in relief from which Niepce was able to make a paper print in an ordinary printing press by applying ink to the raised portion. A print produced in this manner by Niepce in 1824 is shown in Fig. 6.

Niepce was successful this same year in the use of the camera obscura[9] but the exposure required by this process was enormous—from six to ten hours in bright sunlight—and the results were flat and lacking in contrast and detail, so that while Niepce was the first to make a permanent photograph, his process was of little practical value.

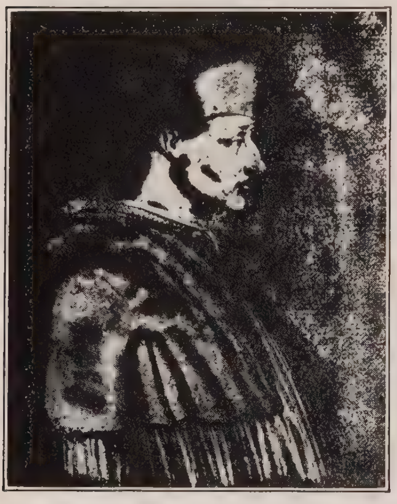

Fig. 6. A Heliographic Print by Niepce, 1824.

Daguerre.—The first to develop a practical process was Louis Jacques Mande Daguerre, who was born at Cormeilles, near Paris, in 1787, and died at Petit-sur-Marne 1851. As a scene painter, Daguerre had used the camera obscura in a series of panoramic paintings of the cities of Europe; and it was undoubtedly this which induced him to undertake the fixing of the image by the action of light on a light-sensitive substance. His investigations began apparently about 1824. Two years later he received word, probably from Chevalier, an optician from whom he had purchased some of the apparatus necessary for his experiments, that the subject was occupying the attention of a man in the Provinces, one Joseph Nicephore Niepce. Daguerre immediately wrote to Niepce suggesting an exchange of secrets, but Niepce was distrustful of Daguerre, who by now was a popular figure in Paris, owing to his invention of the Diorama. Not until 1827, when he met Daguerre while on a trip to his brother Claude in England, were cordial relations established between the two investigators. On December 14, 1829, the two signed an agreement of partnership to continue for ten years, during which each would work to their mutual advantage.

[9] Cromer, *Bull. Soc. franç. Phot.* **9** (1922) 69.

Epstean—Facts about Nicephore Niepce. Phot. J. **80** (1940) 168.
Johnston—Facts about Nicephore Niepce. Phot. J. **80** (1940) 17.

Upon the death of Niepce in 1833, if not before, Daguerre discarded the methods of the older investigator and returned to the silver salts. In 1835 he advised Isidore Niepce, who had succeeded to his father's interest in the partnership, that he had reached a certain amount of success. After two years more spent in perfecting details, a company was formed to buy out the process for the sum of 200,000 francs. They were unsuccessful, however, in obtaining the necessary capital. The failure led the two partners to appeal to Arago, the famous secretary of the Academie des Sciences. Arago reported on what he had seen to the Academie on January 7, 1839, but gave no details of the process. The Diorama, a theatrical venture in which Daguerre had

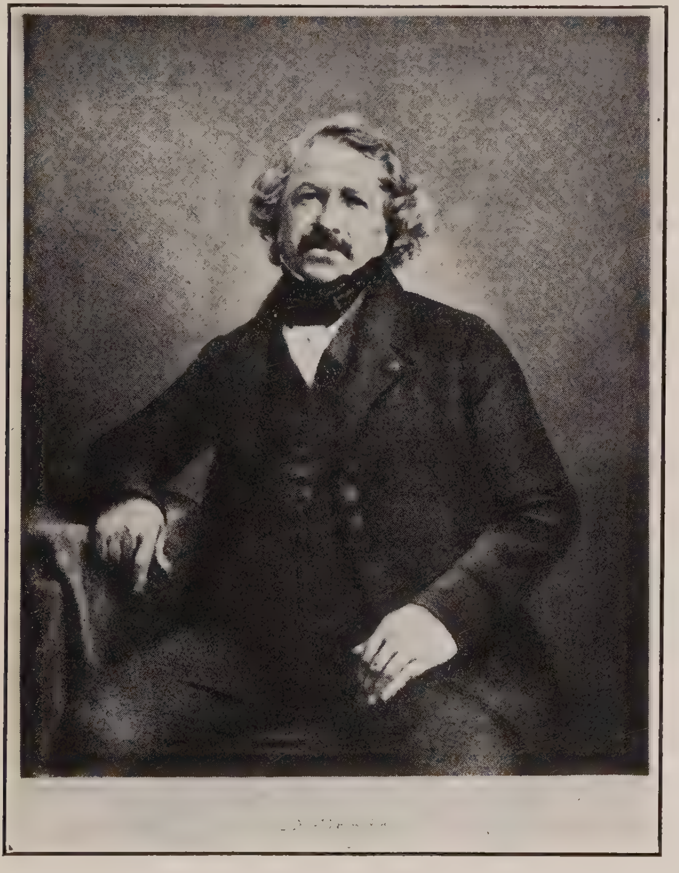

FIG. 7. Jacques Mande Daguerre.

invested heavily, burned on March 8. In July, a bill granting a life pension of 6,000 francs to Daguerre and one of 4,000 francs to Isidore Niepce was presented in the House of Deputies by Arago and supported by Biot and Humboldt, all members of the Academie des Sciences. This bill was passed and received the approval of the King.

Finally on August 18, 1839, the details of the process were made public at a special joint meeting of the Academie des Sciences and the Academie des Beaux-Arts.[10] A silver plate, or a copper plate covered with silver, was polished and then exposed to the vapors of iodine to produce a light-sensitive layer of silver iodide. After an exposure within the camera, which at the time amounted to as much as 10–20 minutes, but was later reduced to a few seconds, the invisible image was brought out or " developed " by exposing the surface of the plate to mercury which is heated. The mercury, by attaching itself to the unexposed portions of silver iodide, produces a positive image. To render the image permanent, the unexposed silver iodide remaining was removed by placing the plate in a solution of common salt (sodium chloride). Salt was soon replaced as a fixing agent by sodium thiosulfate, the properties of which had been published by Herschel in 1819, twenty years earlier.

Daguerre's early plates required an exposure of 10–20 minutes, but the following year Goddard, of London, discovered the superior sensitivity of silver bromide and one year later the exposure was reduced to a few seconds by the introduction by Voightlander of a rapid portrait lens from the calculation of Josef Petzval of Vienna.

Later History of the Daguerreotype.—The Daguerreotype process spread quickly throughout the civilized world and before the close of the year, the process was being worked in all important countries. Daguerre's description of the process *History and Description of the Daguerreotype* published in September 1839 in Paris went through *twenty-six* editions in the next five months and was translated into German, English, Italian and Spanish. The news reached America in the latter part of September. It is not known who made the first Daguerreotype in America. It may have been S. F. B. Morse who had met Daguerre in Paris earlier in the year. The *New York Herald*

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[10] For an interesting account of these proceedings see: Potonniée, *History of the Discovery of Photography*. Translated by Epstean (New York).

Potonniée—Two unpublished documents concerning the history of the daguerreotype. Phot. J. **78** (1938) 28.

described a Daguerreotype of St. Paul's Church in its issue of September 30, 1839.[11]

At first, the Daguerreotype process required from 10 to 20 minutes exposure in bright sun. Daguerre, it appears, had confined himself to outdoor views and had not attempted portraiture up to the time at which the details of the process were divulged, as he regarded the exposure as being too long to make portraits possible. It is not definitely known who first succeeded in making portraits by the Daguerreotype process. A manual of the Daguerreotype process, *Historie et descriptions des procédés de daguerreotype et du diorama rédigés par Daguerre et argumentés de notes et d'observations par M. M. Lerebours et Susse frères,* published in Paris before the close of the year 1839 contains the following: " To take a portrait, it is also necessary to have recourse to a bright light. One will not succeed well except by exposing the person in the sun, in the open air and with reflections from white draperies." Does this mean that the writers were speaking from practical experience and had actually made portraits by the Daguerreo-

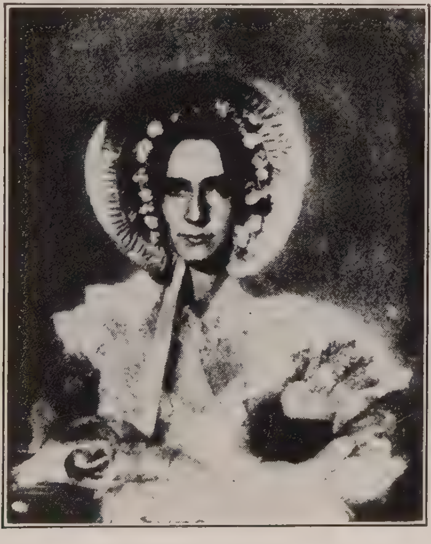

FIG. 8. Daguerreotype Portrait by J. W. Draper of New York, Frequently Considered to be the First Portrait by Photography (1839 or 1840).

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[11] The first manual of photography published in America appears to have been *Description of the Daguerreotype Process,* Gourand (Boston 1840). Authority—Robert Taft, *Photography and the American Scene.* Macmillan (New York 1938).

type process? One wonders.[12] The claims of Morse, Draper and Wolcott in America have been investigated in detail by Taft.[13]

Briefly, the facts appear to be as follows: Morse wrote Daguerre on November 19, 1839, that he had thus far had only indifferent success. Draper, in a letter dated March 31, 1840 to the *Philosophical Magazine* of London, claimed to have achieved success in December 1839. The daguerreotype referred to was the well-known portrait of his sister (Fig. 8) often referred to as the first portrait by photography. Alexander Wolcott, an instrument maker of New York City, soon after the publication of the details of the process, constructed a camera using a concave mirror of large diameter and short focus and thus obtained a much brighter image than was produced by the lenses available at the time. With this he claimed to have made a Daguerreotype portrait in October 1839. Details of his equipment were published in the *American Repertory* for April 1840. He opened a studio for the making of Daguerreotypes in New York City on March 4, 1840. This was possibly the first commercial photographic establishment in the United States.

Meanwhile in Europe, important technical advances were being made. The time of exposure was reduced materially (1) by the substitution of silver bromide for silver iodide, an advance due to John Frederick Goddard of London in 1840,[14] and (2) by the portrait lens of Joseph Petzval which was introduced by Voightlander the same year.

While they contributed nothing of importance to its development technically, American workers were second to none in their mastery of the process. The preeminence of such Daguerreotypers as Hawes and Whipple in Boston, the Langenheim Brothers in Philadelphia and Matthew Brady in New York, seems to have been admitted even in England and the Continent. Possibly due to this fact, the Daguerrotype process remained in use longer in the United States than in other countries. Even as late as 1865, Daguerreotypes were still being made professionally in the United States, although the process had largely given way to collodion both in this country and abroad in the middle fifties.

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[12] J. B. Reade in 1854 in the *Journal of the Photographic Society* of London claimed that Talbot made a portrait before 1839. This seems incredible in view of the time of exposure required by his process. *Amat. Phot.* **80** (July 1935) 69.

[13] Taft, *Photography and the American Scene*. Macmillan (New York 1938).

[14] This discovery seems to have been made independently by Paul Beck Goddard of Philadelphia in December 1839.

William Henry Fox-Talbot.—Meanwhile, in England, William Henry Fox-Talbot (1800–1877) was assiduously engaged in an attempt to fix the image of the camera obscura. Talbot relates in his *Pencil of Nature,* published in 1844, that in 1833 he was sketching with a camera obscura on the shores of Lake Como but without much success, owing to his inability to draw well. Returning to England in January of the following year, he determined to follow up the work of Wedgwood and Davy. His first experiments were unsuccessful as the paper was not sufficiently sensitive to light. Later (1835) he found that the sensitiveness of the paper was greatly increased by giving it successive washings, first with a solution of common salt, then a solution of silver nitrate and finally exposing it while still wet. In addition, he found that a strong solution of common salt would dissolve the unexposed silver chloride and render the image permanent. With paper so prepared, he made a photograph of his home, Lacock Abbey, the same year (1835). This was apparently the first permanent negative

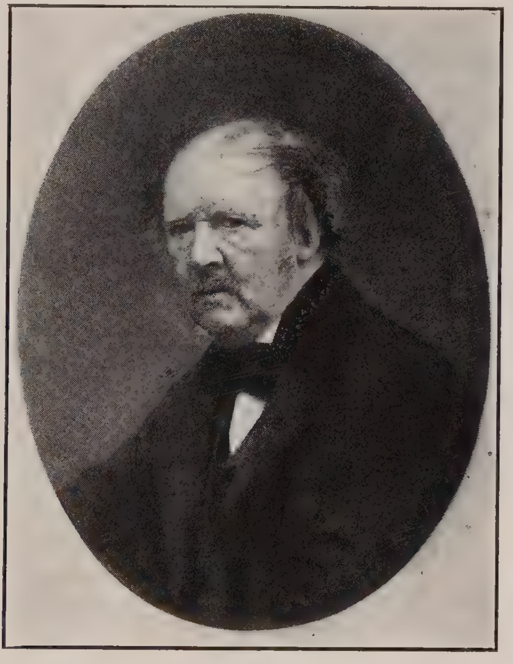
Fig. 9. William Henry Fox-Talbot.

image produced in the camera. Talbot did not publish the results of his work immediately, desiring to perfect the process, but upon news from Paris of Daguerre's discovery he sent a brief communication of the process, which he termed *Photogenic Drawing,* to the Royal Institution, and a week later (January 31, 1839) Talbot himself read a paper on his process before the Royal Society. This, it will be noted, was almost eight months before the details of the Daguerreotype process were made public.

In 1841 Talbot patented his *Calotype* (beautiful picture) process. In this process thin, transparent paper was first soaked in a solution containing silver iodide, and then immediately before exposure it was washed over with a solution of gallic acid and silver nitrate. After an exposure of about one minute, the paper was developed in gallic acid. Talbot had at last grasped the idea of a developer for bringing out a latent invisible image and thus reducing the exposure. After fixing and drying, prints were made by exposing another sheet of paper underneath the negative, developing in gallic acid, and fixing in hypo.

Talbot's method was never widely adopted for professional use as the images were not as sharp and clear as the Daguerreotype and because the process was protected by patents and a license had to be obtained from the inventor. The Daguerreotype was, of course, free to all since the French Government had awarded life pensions to Daguerre and Niepce on condition that the invention be published without patent. Talbot attempted to prevent the practice of the Daguerreotype process professionally in England as an infringement of his patent, but was defeated.

Talbot's process, however, was much cheaper and was used by many amateurs. It was used also for a series of remarkable portraits by the Scotch painter, D. O. Hill, and his assistant, Robert Adamson, a chemist, during the years 1843 to 1848. These portraits, two of which

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Clerk-Maxwell—The Personality of Fox-Talbot. Phot. J. **76** (1936) 429.

Lambert—Fox-Talbot's Photographic Inventions. Phot. J. **76** (1936) 431.

Johnson—Sidelights on Fox-Talbot. Phot. J. **81** (1941) 24.

Wight—Early Photographic History in Scotland. Phot. J. **81** (1941) 15.

Brown—Makers of Photography. British Journal Photographic Almanac (1931) 145.

Talbot—The Life and Personality of Fox Talbot. Phot. J. **79** (1939) 546.

are reproduced in Figure 10, rank with the best that have ever been produced by photography.[15]

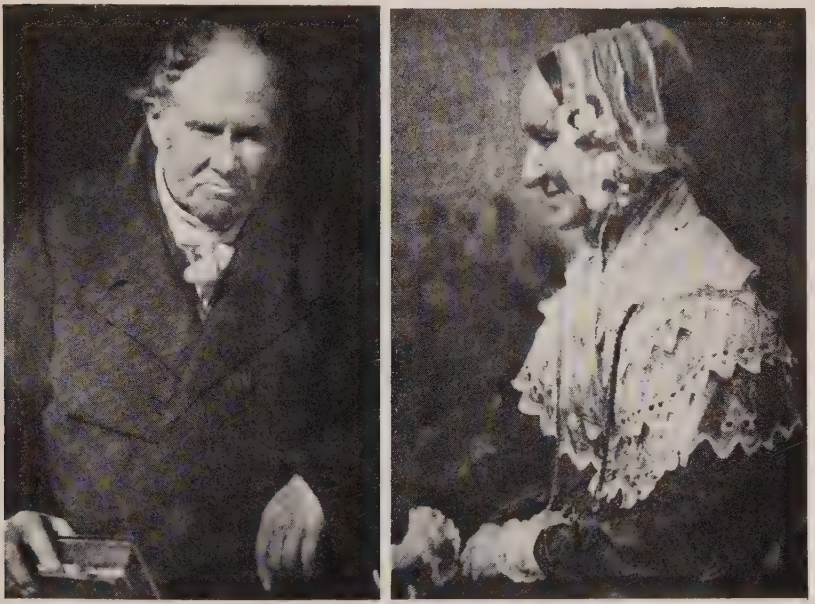

FIG. 10. Calotype Portraits by D. O. Hill.

Negative Processes on Glass.—Paper is not altogether satisfactory for negatives and as early as 1839, a Dr. Fyfe of Edinburgh suggested the use of glass and a " varnish " to hold the silver halide. The following year, Sir John Herschel[16] attempted to prepare sensitized glass plates by precipitating silver chloride on glass but obtained only faint images. In 1847, Niepce de St. Victor, a cousin of Nicephore Niepce, succeeded in obtaining satisfactory images on glass coated with albumen. Wolcott[17] in the United States experimented with albumen in 1847 but was unsuccessful.

Three years later (1850) Whipple, a professional photographer of Boston, patented a process employing glass plates coated with milk and albumen. Le Gray in France suggested the use of collodion—guncotton dissolved in alcohol and ether—the same year, but the suggestion received little attention. A year later, Frederick Scott-Archer (Fig. 11) in London published the details of a process employing collodion which was so perfect that it soon superseded all other processes of photography and even today is in general use in certain fields as, for example, in the making of the negatives used in making half-tone engravings for letter press printing.

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[15] For an interesting account of the life and work of D. O. Hill see Wight, Early Photographic History in Scotland—D. O. Hill. *Phot. J.* **81** (1941) 11.

[16] *Proc. Royal Society* Feb. 20, 1840.

[17] Taft, *Photography and the American Scene.*

Fig. 11. Frederick Scott-Archer. (Portrait from J. Werge, *The Evolution of Photography*.)

Archer's process is termed wet-collodion because the glass must be coated, the exposure made and developed before the collodion has dried. A clean glass plate was first coated with collodion to which a soluble iodide, such as potassium iodide, had been added. The plate was then sensitized by immersion in a bath of silver nitrate, exposed in the camera while still wet and developed at once, using a solution of pyrogallol and silver nitrate, and finally fixed in sodium thiosulfate, or hypo. At no stage in the process may the collodion become dry or the picture will be lost; hence, when making pictures out-of-doors, it was necessary to take along a dark tent in which to prepare the plate and, after the exposure, to develop it. Some idea of the labor and inconvenience involved in making a photograph in those days can be obtained in Figure 12 which shows the pack carried by the photographer and Figure 13, the photographer at work in the field.

In the years which followed, attempts were made to prepare plates which would keep and thus avoid the necessity for a darkroom when making pictures away from the studio. Most of these processes involved the addition of hygroscopic substances to prevent the collodion from drying. The most successful of such processes were those of Taupenot (1855) in France and Norris (1856), of Birmingham. In the first, the plate, after having been coated with collodion in the usual manner, was coated a second time with albumen and then allowed to dry. It was then immersed in a bath of silver nitrate, washed and dried. The process patented by Norris was similar except that gelatin was employed in place of albumen.

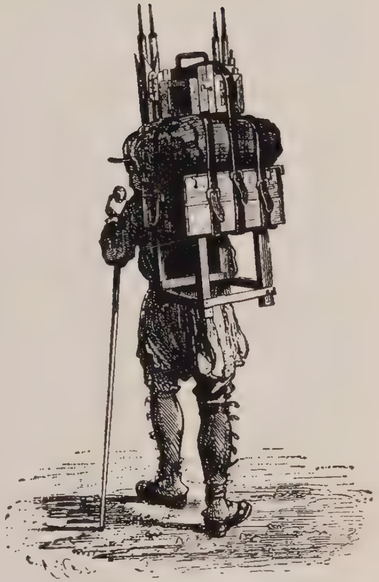


FIG. 12. Wet-Plate Photographer with Equipment for Outdoor Photography. (From Thomson, *A History and Handbook of Photography.*)

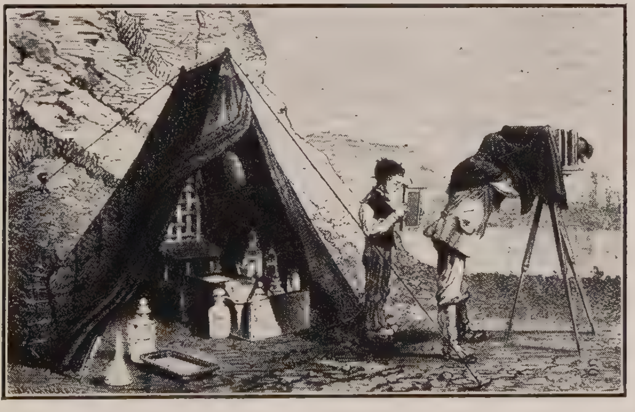


FIG. 13. Wet-Plate Photographer at Work in the Field. (From Thomson, *A History and Handbook of Photography.*)

In 1864 Sayce and Bolton discovered a practical means of preparing a collodion emulsion. To prepare a so-called emulsion (photographic emulsions are in reality suspensions) silver nitrate was added to iodized collodion; this produced silver iodide by precipitation rather than by immersing the collodion-coated plate in a solution of silver nitrate. After coating, the plates were immersed in a solution of tannin which acted as a preservative and maintained the permeability of the collodion. All of these processes were considerably slower than wet-collodion and did not find much acceptance except among landscape photographers.

Gelatin Emulsion.—The first recorded application of gelatin to photography is the unsuccessful attempt of Niepce de Saint Victor to use gelatin as a vehicle for holding silver iodide to glass plates. Gelatin, however, became soft and frequently left the glass when the plate was placed in the nitro-acetic silver bath used for sensitizing and was discarded, for albumen. Attempts were made by Gaudin (1853) to prepare what might be termed gelatino-iodide emulsion but his process was not practical.

In 1868 W. H. Harrison described a method of emulsifying silver bromide in gelatin which was not entirely satisfactory and appears to have received little attention. Three years later, R. L. Maddox (Fig. 14), an English amateur, published—also in the *British Journal of Photography*—a method of preparing gelatin dry plates but as he employed an excess of silver when precipitating the silver bromide and did not appreciate the importance of washing to remove the excess silver salts, the emulsion was slow and suitable only for contact printing. Maddox was more fortunate than Harrison, however, for his process, imperfect though it was, seems to have attracted some attention.

Two years later, J. Burgess advertised gelatin emulsion with which photographers could coat their own plates. While the venture was not successful financially, Burgess proved that excellent results could be obtained with gelatin emulsion and really deserves to be regarded as having produced the first practical gelatino-bromide emulsion. Burgess apparently recognized the need of washing the emulsion to remove the superfluous salts and possibly also the desirability of an excess of soluble halide rather than silver in the formation of the silver bromide, but his process was never published and it remained for Johnson and King independently to call attention to these points the following year.

In 1874, gelatin-bromide dry plates were placed on the market in England by the Liverpool Dry Plate Company. The term, *dry* plate, was adopted to distinguish the process from wet-collodion. Four years later, Bennett of London found that the sensitivity was increased considerably by heating the emulsion to a temperature of from 90 to 95° F., and the following year (1879) Mansfield showed that still greater sensitivity might be obtained by precipitating the silver bromide in a *part* of the gelatin, boiling the emulsion thus prepared for a few minutes and then adding the remainder of the gelatin at a lower temperature. While gelatin dry plates had already begun to replace the wet-collodion process, the procedure of Mansfield so greatly increased the sensitivity of gelatino-bromide emulsion that it soon replaced the older process everywhere.

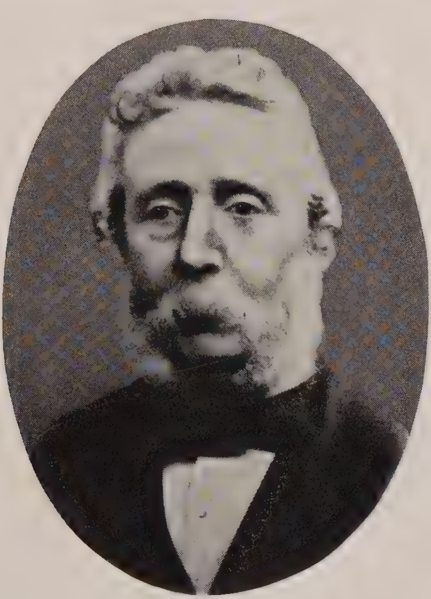


FIG. 14. Richard Leach Maddox, One of the Pioneers in the Introduction of Gelatin Emulsions.

The favorable influence of ammonia on sensitivity was observed by the Belgian, Monkhoven (1879), and shortly thereafter Eder, of Vienna, perfected a process for the preparation of gelatino-bromide emulsion of high sensitivity using ammonia or ammonium carbonate. Abney, in England, called attention to the advantages of employing a small amount of silver iodide in a gelatino-bromide emulsion.

By this time (1879) manufacturers of dry plates were established in England, Germany, the United States and Belgium. The manufacture of dry plates in England began, as we have seen, with the Liverpool Dry Plate Company in 1874, to be followed by Wratten and Wainwright in 1877 and many others in the next few years. In the United States, the manufacture of dry plates was begun by Carbutt of Philadelphia in 1879, who was followed a year later by Eastman in Rochester, Cramer of Saint Louis, Cross of Indianola, Iowa and Anthony of New York. The Eastman plates appear to have been the first to be coated by machinery, Eastman having been granted a U. S. patent for an emulsion coating machine on April 13, 1880. In Germany, dry plates were placed on the market by Johann Sachs and Company (Berlin) and F. Wilde in Goerlitz (1879).

Emulsion Supports for Negative Purposes.—Paper was used as a support for the emulsion until 1851 when the wet-collodion process of Scott-Archer using glass plates was introduced. Efforts to replace glass began in 1877 when Palmer was successful in preparing flexible films of gelatin on which the emulsion might be coated. These, however, were not successful commercially. Gelatino-bromide emulsion on layers of hardened gelatin or collodion was placed on the market between the years 1879 and 1881 by Stebbing, Ferrier and Pumphrey. In 1884 Eastman in America patented stripping film. This stripping

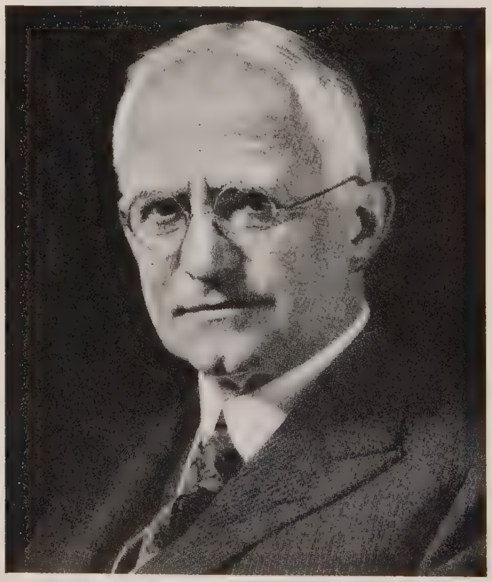


Fig. 15. George Eastman, Founder of the Eastman Kodak Company.

film consisted of paper coated with a thin layer of soluble gelatin which in turn was coated with a gelatino-bromide emulsion. After developing and fixing, the image was stripped from the paper support and dried on glass. This film was supplied in rolls and a roll holder was provided to adapt it to the plate cameras then in common use. From the standpoint of the general public this was a great advance, but the process was still intricate and difficult for the amateur because of the delicate handling demanded in transferring the image from the paper to the final glass support. Five years later (1889) the stripping film with its paper base gave way to a transparent base of nitrocellulose introduced by the Eastman Dry Plate and Film Company of Rochester, New York, U. S. A. The introduction of a daylight loading camera two years later (1891) brought photography within the reach of all.[18]

History of Color Sensitizing and Color Sensitive Materials.—The sensitivity of the silver halides lies almost exclusively in those portions of the spectrum which produce the visual sensation of blue and violet and in the invisible ultra-violet. In 1873, Vogel of Berlin observed that a certain collodion emulsion which had been dyed with a yellow dye to prevent halation had a different sensitivity from those which had not been dyed. This effect was traced to the dye and thus was discovered the principle of dye sensitizing. Continuing his investigation, Vogel found a number of dyes which act as sensitizers, the most important being cyanine and quinoline red (1884) neither of which is in use today. In 1874, Waterhouse of London found that eosin was a yellow-green sensitizer for collodion emulsion and Clayton and Tallifer patented in England and France its use with gelatin emulsion.

[18] Hannibal Goodwin, a minister of Newark, New Jersey, filed an application for a U. S. Patent on a method of preparing a "photographic pellucle" from nitrocellulose May 2, 1887. After the original application had been several times amended, a patent was granted September 13, 1898. In the meantime, H. M. Reichenbach, an employee of the Eastman Company, applied for, and was granted, a patent for a nitrocellulose film base December 10, 1889. The first film was placed upon the market by the Eastman Dry Plate and Film Company on August 27, 1889. Goodwin's patent was acquired in 1902 by the Goodwin Film and Camera Company, which brought suit against the Eastman Company for patent infringement. In 1914, the courts upheld the validity of the Goodwin patent and the Eastman Kodak Company settled with the Ansco Company, the owners of the Goodwin patent, for $5,000,000 in cash. See: Ackermann—George Eastman (Houghton Mifflin 1930). Taft—Photography and the American Scene (Macmillan 1938).

THEISEN—The History of Nitrocellulose as a Film Base. J. Soc. Mot. Pict. Eng. **20** (1933) 259–266.

Eder of Vienna found that erythrosin, the iodine analogue of eosin, was still better and for a number of years it was the best known sensitizing dye for the green region. Shortly thereafter, dry plates sensitized with erythrosin were placed on the market by most manufacturers as *orthochromatic* or *isochromatic plates.*

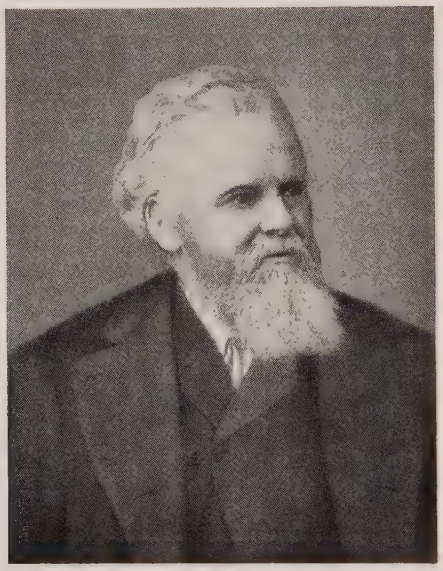


FIG. 16. H. W. Vogel, Discoverer of Dye Sensitizing.

In 1902, Miethe and Traub discovered the sensitizing properties of Ethyl red, an analogue of cyanine, and the following year, Koenig of the Hoechst dye works introduced in rapid succession a number of yellow and green sensitizers, the more important being Orthochrome, Pinaverdol, and Pinachrome. A satisfactory red sensitizer was not discovered until 1906 when Homolka, of the Hoechst dye works, discovered a carbocyanine dye which was introduced as Pinacyanol. Panchromatic plates sensitized with pinachrome and pinacyanol were placed on the market in 1906 by the firm of Wratten and Wainwright in England.

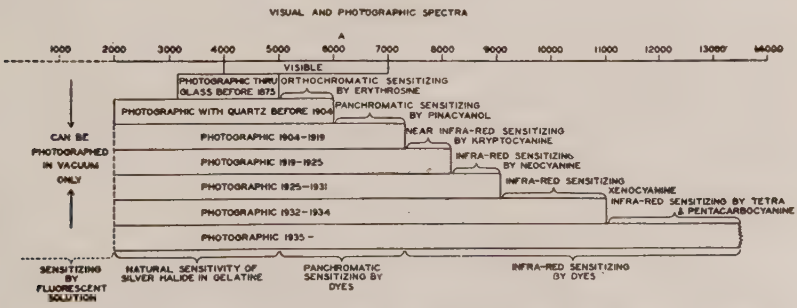
In recent years the work of Mills, Hamer, Pope, Brooker and others has made available a number of new sensitizers much more efficient than those previously known. These new sensitizers have the advantage over the older sensitizers of not lowering the general sensitivity of the emulsions nor increasing fog. In fact with some, fog is less than with the same emulsion not color sensitized. This is particularly the case with slow, fine-grain emulsions. The introduction of panchromatic materials of the hypersensitive and supersensitive types in 1928–1930 marks a new epoch in the history of photographic negative materials.

Shortly after the introduction of Pinacyanol, the Hoechst dye works discovered the first sensitizer for the infra-red, Dicyanine. This, while a good sensitizer for the infra-red, is unstable and tends to fog badly so that in practice it cannot be relied upon to yield satisfactory results.

In 1919, Adams and Haller of the U. S. Bureau of Chemistry prepared a new dye similar chemically to pinacyanol but sensitizing specifically in the infra-red with a maximum action of 750 mμ. This was termed kryptocyanine. It was many more times powerful as a sensitizer for the near infra-red than Dicyanine and quite free from fogging tendencies. In 1925, H. T. Clarke of the Kodak Research Laboratories separated a new dye from kryptocyanine with a maximum at 850 mμ. This was termed Neocyanine.

The sensitizing properties of the tricarbocyanine dyes were discovered in 1930. The sensitizing action of these extends much further into the infra-red; Xenocyanine, described by Brooker, Hamer and Mees, sensitizes to 1100 mμ with a maximum at 980 mμ. Still more recently (1935) an investigation of the tetra- and pentacarbocyanines by Brooker, Keyes, Koenig and others has resulted in the discovery of several dyes whose sensitizing action extends still further into the infra-red. These have made possible the photography of spectral lines beyond 1300 mμ. The discovery of efficient sensitizers for the infra-red such as Kryptocyanine, Neocyanine and Xenocyanine has made possible infra-red sensitive plates and films suitable not only for spectrography but for general photography, the motion picture industry and aerial photography.

The following chart [19] illustrates diagrammatically the progress which



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[19] This diagram represents a modification of one used by Mees. *Nature* 137 (1936) 729.

has been made in the sensitizing of photographic materials since 1873 insofar as the spectral range is concerned.

History of Developing Substances.—The existence of a latent image and the possibility of converting such an image into a visible one through chemical treatment appears to have been discovered by Daguerre, who quite by accident found that mercury was attracted by the exposed silver halide thus converting an invisible image into a visible one.

Talbot introduced the use of a solution of gallic acid as a developer for silver chloride with his Calotype process (1841) although its properties had been discovered some years previously by an English clergyman and microscopist, the Rev. J. B. Reade.

The oldest of the developing agents now in general use is pyrogallol, which was introduced by Scott-Archer with his wet collodion process in 1852. Pyrogallol was not used in an alkaline solution, however, until 1862, nor was sodium sulfite used as a preservative until 1882.

Ferrous sulfate was introduced by Hunt in 1844 and remained in general use until the wet-collodion process was superseded by gelatino-bromide emulsion. Even then it continued to be used by many of the older workers for some years.

The developing properties of hydroquinone were discovered by Abney of London, in 1880, and those of pyrocatechin, which is closely related chemically, by Eder and Toch, of Vienna, the same year.

The years between 1888 and 1900 witnessed great activity in the field of developing agents; the developing properties of paraphenylene diamine were discovered in 1888 by Andresen. A year later Andresen introduced Eikonogen (sodium-amido-β-naphthol-β-sulfonic acid) whose properties as a developer had been discovered by Meldola. Two years later (1891) the firm of Hauff introduced *Metol* (monomethyl paraminophenol sulfate). This was followed by diaminophenol or *Amidol* (1892); *Ortol* (a combination of hydroquinone and methyl-ortho-aminophenol) in 1896 and *Adurol* (monochloro-hydroquinone or chloroquinol) in 1898. Eikonogen has been superseded by metol, and Ortol is but little used today, but the other three remain in general use with Metol the most popular. *Edinol,* the sulfate of oxymethyl paraminophenol, was introduced by Bayer in 1901.

The Brothers Lumière are responsible for a number of developing agents; *Metoquinone,* a chemical mixture of Metol and hydroquinone (1903); *Chloranol,* a combination of hydroquinone and methyl-paraminophenol (1913); and *Hydramine,* a chemical combination of hydroquinone and paraphenylene (1899).

Among organic developing agents no longer available but once popular may be mentioned *Duratol,* a benzyl-paramenophenol, introduced by Schering in 1910; *Diogen,* introduced by Agfa (1893) and said to be sodium-alpha-amido-naphthol-disulfuric acid; *Monomet* (para-amido-ortho-cresol-hydrochloride), introduced in England by the White Band Company 1916, and *Neol,* introduced by Hauff in 1918 and stated to be para-aminosalicylic acid.

Alkaline development appears to have been discovered by Major Russell and Leahy independently (1862). Ammonia was first used but was later replaced by the caustic alkalis and the alkaline carbonates such as sodium carbonate. The use of sodium tribasic phosphate was suggested by Lumière in 1906 and is finding some favor today in fine grain developer formulas. Acetone and formaldehyde were introduced by Lumière in 1896 and 1898. The former is now seldom used but formaldehyde is used in a number of developers for use with films designed for photo-mechanical purposes. Borax and certain related compounds have come into general use in recent years in fine grain developers. The first developing formulae of this type to become popular were those of Wellington and Capstaff.[20]

The use of sodium sulfite as a preservative in solutions of organic developers appears to be due to Berkley (1882). Acid sulfites such as potassium meta-bisulfite and sodium bisulfite were recommended by Mawson and Swan (1887).

Development of Printing Processes with Silver Salts.—For printing from negatives made by his Calotype process, Talbot employed what we term today the salted paper process. Paper of suitable surface is immersed in a weak solution of salt, after which it is dried. Just before use, it is sensitized by immersion in a solution of silver nitrate and dried, exposed to light beneath the negative until sufficiently dark and fixed in hypo. Le Gray introduced the toning of the print with gold chloride as a means of improving the color in 1849.

The incorporation of albumen with the salting solution to keep the silver salts on the surface and give the paper a gloss finish appears to have been suggested by Le Gray or by Blanquart-Evrard (1850). For more than 30 years, albumen paper was practically the only process of printing in general use. Paper coated with albumen was supplied ready for sensitizing in a solution of silver nitrate by the photographer. In

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[20] Capstaff and Seymour, *Amer. Phot.* 21 (1927) 98.

1870 Adolph Ost of Vienna discovered that the addition of a citrate enabled the sensitized paper to be kept for several months which made it possible to supply the photographer with ready-sensitized paper.

A method of using collodion in place of albumen was described by G. Wharton Simpson in 1865 and collodio-chloride of silver papers were introduced commercially by Obernetter, of Munich, two years later, but the process did not attract much attention until the introduction of a much improved product by Liesegang, of Duesseldorf, in 1886.

Gelatino-chloride papers appear to have been first employed by Palmer and Smith as early as 1866, but no details were published. Full details for the preparation and use of gelatino-chloride papers were published by Abney in 1882 and were introduced commercially two years later by Obernetter, of Munich, and a few years later by Liesegang, of Duesseldorf, and Ilford, of London.

The above papers are all members of the class known as printing-out papers; that is, they produce a visible image upon exposure and there is no after development. The now popular developing papers appear to have had their prototype in a process used by Blanquart-Evrard (1851), but it was not until 1874, after paper coated with gelatino-bromide emulsion had been introduced by the Liverpool Dry Plate Company, that developing papers made any headway. In 1880 Morgan and Kidd established a factory at Richmond (England) and in 1884 Eastman, of Rochester, introduced the machine coating of paper in the roll with gelatino-bromide emulsion, after which gelatino-bromide paper began to assume importance as a printing process.

Directions for the preparation and use of developing emulsions of silver chloride for positive printing were published by Eder and Pizzighelli in 1881. The first papers of this type were introduced commercially by Dr. E. Just, of Vienna, in 1883 and shortly afterward in England by Edwards and Warneke, but " Velox," introduced in America by the Nepera Chemical Company from the formula of Dr. Leo Baekeland, was the first to achieve wide popularity. Its successful introduction paved the way for a large number of similar papers in all important countries.

The use of gelatino-chloro-bromide emulsions for positive prints was introduced also by Eder and Pizzighelli in 1883. Chloro-bromide emulsions are especially adapted to the production of warm-tone images and papers of this type are widely employed for portrait work at the present time.

Platinum Printing Processes.—The sensitiveness of certain compounds of platinum especially in the presence of an organic salt, such as ferrous oxalate, was observed by Herschel in 1832. Robert Hunt, in 1854, attempted to develop a printing process employing platinum chloride and ferric oxalate but was unsuccessful. The first practical process was patented by William Willis of London in 1873. In this process, paper coated with potassium chloroplatinite and ferric oxalate is exposed under the negative until a faint image appears. It is then placed in a solution of potassium oxalate, in which the reduced iron salt is soluble, and as it is dissolved by the oxalate, it attacks the platinum compound reducing it to the metallic state.

A direct printing out process requiring no development was perfected by Hubl and Pizzighelli but has never been widely used.

Printing Processes Employing Compounds of Chromium.—The observation that certain compounds of chromium are sensitive to light appears to be due to Mungo Ponton, an Englishman, who in 1839 discovered that paper soaked in a bichromate and dried was sensitive to light. The following year Becquerel found that gelatin, gum, and similar substances are rendered insoluble when exposed to light in the presence of a bichromate. In 1855 Alphonse Poitevin patented a process of printing in which paper with a layer of gelatin containing a pigment was sensitized in potassium bichromate and exposed to light. Then upon washing in water, the soluble gelatin in the unexposed portion washed away leaving an image formed by the pigment held in the insoluble gelatin. Poitevin's results were unsatisfactory as were those of John Pouncy, of Dorchester, who patented a similar process in 1858.

Laborde the same year pointed out that in the half tones only the upper portion of the gelatin layer is rendered insoluble on exposure and, as the lower strata remain soluble, the image washes away. To avoid this, Blair, Burnett and Schouwaloff independently and almost at the same time (1858) suggested that the exposure be made through the paper so that the exposed layers would lie next to the base of the paper. Fargier in 1860 coated the exposed film with collodion and then washed away the soluble gelatin from the back. Pigment printing was placed on a practical basis by Swan when he patented carbon tissue in 1864. The carbon tissue, which is simply paper coated with gelatin and a suitable pigment, is sensitized with a bichromate, dried and exposed. The gelatin layer is then transferred to another support thus placing the soluble gelatin on the surface from which it is removed by washing in water.

Gum-bichromate is a non-transfer process of pigment printing based upon the original work of Poitevin and Pouncy. Washing away of the highlights is to a large extent prevented by using a thin layer of pigmented gelatin and building up an image by successive printings. The process was brought to the front about 1895 largely as a result of the pictorial work of Demachy, Puyo and other French pictorialists.

Marion, in 1873, found that paper immersed in a solution of potassium bichromate, dried and exposed to light under a negative so as to form a faint image, will transfer the image to a sheet of carbon tissue left in contact with it for some time. Manly in 1899 patented a similar process which was termed *Ozotype* and in 1905 another known as *Ozobrome*. In the latter, a sheet of carbon tissue was soaked in a solution of potassium bichromate, ferricyanide and bromide. The sheet of carbon tissue is placed in contact with a bromide print for several minutes, transferred to another support and developed by washing in water as usual. The bromide print thus takes the place of the negative and there is no exposure to light. Ozobrome was revived in an improved form by H. F. Farmer in 1919 as *Carbro*—carbon from bromides—and has proved quite successful.

The Development of the Oil, Bromoil and Powder Processes.—A second process was worked out and patented by Poitevin in which a bichromated gelatin film *without pigment* was exposed under a negative. This gelatin film upon exposure to light under the negative became more or less insoluble in various portions according to the gradations of the negative. When immersed in water, the soluble gelatin absorbs water and becomes so charged with water that it will repel a greasy ink, while the shadows, being insoluble, do not absorb water and will accept the ink. Accordingly when a roller charged with greasy ink is passed over the print, an image is formed in greasy ink which adheres to the shadows but not to the highlights of the print. This process was the forerunner of a number of photo-mechanical processes, which are beyond the scope of this work, and the oil, bromoil and powder processes.

Two years before (1853) the Duc de Luynes through the Société Française de Photographie had offered a prize of 10,000 francs to the person discovering a process by which absolutely permanent prints might be produced. The President of the Société, M. Regnault, the famous chemist, in announcing the offer called attention to the permanency of carbon and suggested that experiments be conducted with a view to obtaining prints in carbon. Two Frenchmen, Garnier and Salmon, starting from Poitevin's patent of 1855 worked out a process in which the bichromated gelatin was exposed to light under the negative, soaked in water, and then pure finely divided carbon dusted over it. The carbon adheres only to the unexposed parts and in this way an image is secured. This was the beginning of the so-called powder processes.

Rawlings' process of oil printing (1904) is actually little more than a modification of the process covered by Poitevin's patent of 1855. Rawlings advised the use of brushes rather than a roller for applying the ink; thus it was possible to control the various tones of the print by varying the amount of ink deposited. This feature served to attract various workers who wished to have a ready means of altering the tone values of their prints and the process rapidly gained in popularity among pictorialists.

In 1889, Howard Farmer found that when a gelatin film containing finely divided silver, as in a negative or positive, is immersed in a bichromate, the gelatin in contact with the metallic silver is rendered insoluble exactly as though it had been exposed to light in these portions. Upon this property of a bichromated colloid is based the bromoil process. The first suggestion of the rationale of this process is due to E. J. Wall. It was taken up and worked out practically by C. Welborne Piper.

The Development of the Camera.—Nicephore Niepce, writing in 1816, describes what was probably the first photographic camera as

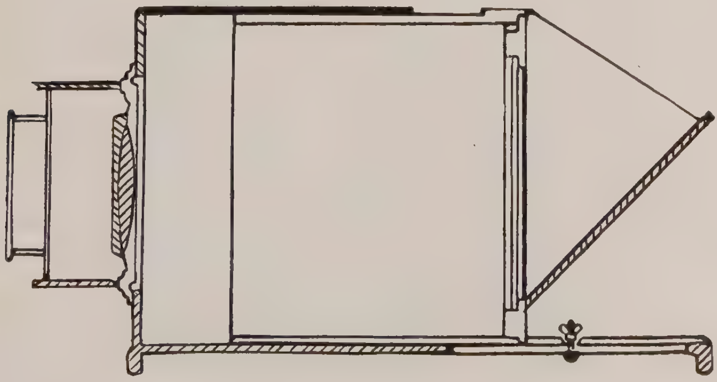

Fig. 17. Drawing of a Camera Described by Daguerre.

being a box about six inches square with a sliding tube carrying the lens.[21]

A camera used by Daguerre consisted of two wooden boxes (Fig. 17) one sliding within the other for focusing the image. A mirror placed behind the ground glass enabled the image to be seen in its correct position (i.e. "right side up").

After the publication of the process there was a demand for cameras similar to that used by Daguerre, who thereupon granted a license to Alphonse Giroux of Paris. To this firm, therefore, belongs the distinction of being the world's first camera makers. In 1840, Voightlander and Sohn, then in Vienna but now at Brunswick, built a portable camera of two sliding metal tubes (Fig. 18). Since this firm is still in existence, this makes it beyond doubt the oldest maker of photographic cameras in the world today.

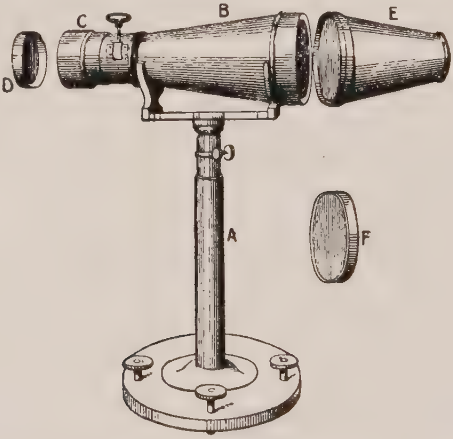

FIG. 18. Metal Camera for the Daguerreotype Process by Voightlander in 1840.

In the period between 1850 and 1860, the photographic camera began to assume the appearance of the familiar view camera of today, although it was much larger, heavier, and clumsier to use. Rising and sliding fronts appear to have been the first of the now familiar adjustments adopted generally, but by 1860 the swing back had appeared. This was followed much later by the reversing back and still later by the swing front. Stand and portrait cameras have not changed fundamentally in design in the last twenty-five years despite the different types and constructions that have been evolved.

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[21] It is reasonably certain that a camera with a bellows was used by Niepce; at any rate, one reputed to have been used by him is in the museum of his home town, Chalons-sur-Saone. Baron Pierre Armand Siguier described and apparently had constructed a bellows camera in 1840, but cameras of this type did not become general until several years later.

While a small camera for instantaneous exposures in the hand was designed by Skaife in 1858, there was little interest in hand cameras until the late seventies when wet-collodion had begun to give way to gelatino-bromide dry plates. Because the earliest hand cameras were intended principally for making pictures without attracting the attention of the subject, they were usually disguised as books, as opera glasses, or hidden in the hat or under the vest (Fig. 19). Shortly thereafter magazine cameras appeared. These were so designed that a number of plates might be placed in the camera and exposed before reloading. Various devices were employed for changing the plates; one of the best known is shown in Fig. 20.

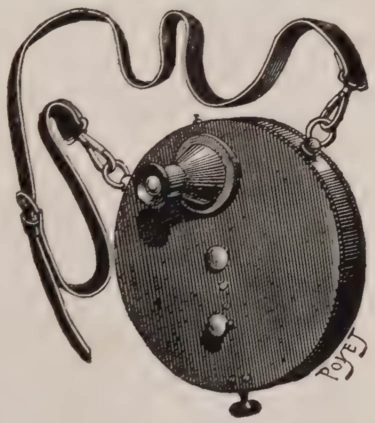


Fig. 19. A Pioneer "Candid" Camera. (About 1875.)

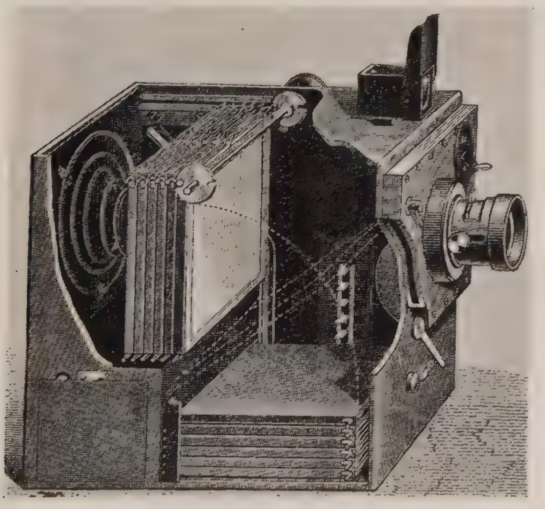


Fig. 20. "Magazine" Camera Enabling Several Exposures to be Made on Glass Plates Without Reloading the Camera.

Many of the features of the reflex camera were anticipated in a camera designed by Thomas Sutton of England in 1860. In this camera, the image was reflected to a horizontal focusing screen by a mirror which was swung up out of the way before making the exposure. The primary purpose of the design was to enable the image to be seen "right side up" on the focusing screen and the interconnection of the mirror and the shutter which forms an integral part of the modern reflex camera was not envisaged by Sutton. A similar design in which the mirror was made to serve as a shutter was patented by Manerizzi of Trieste in 1884. C. R. Smith of London patented the same year what may be termed the first practical reflex camera.

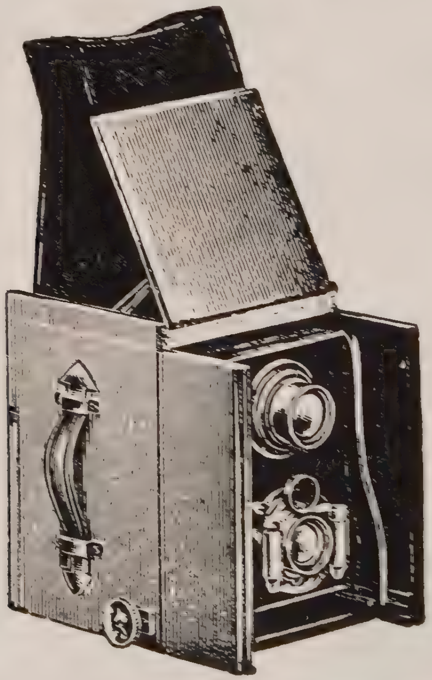


Fig. 21. Early Form of Twin-lens Camera (1900).

The combination of two cameras, one to serve for focusing and arranging the image, the other for making the picture, appears to have originated with Desderi in 1864. Before the introduction of the reflex camera in the early years of this century, twin lens cameras of the type shown in Fig. 21 were popular despite their size and weight. Within recent years, this type of camera has been revived in smaller sizes and is once more in general use.

The first hand camera designed exclusively for roll film was the Kodak of George Eastman which was placed on the market in 1888. It was a box camera (Fig. 22) making 100 pictures 2½ inches in diameter.

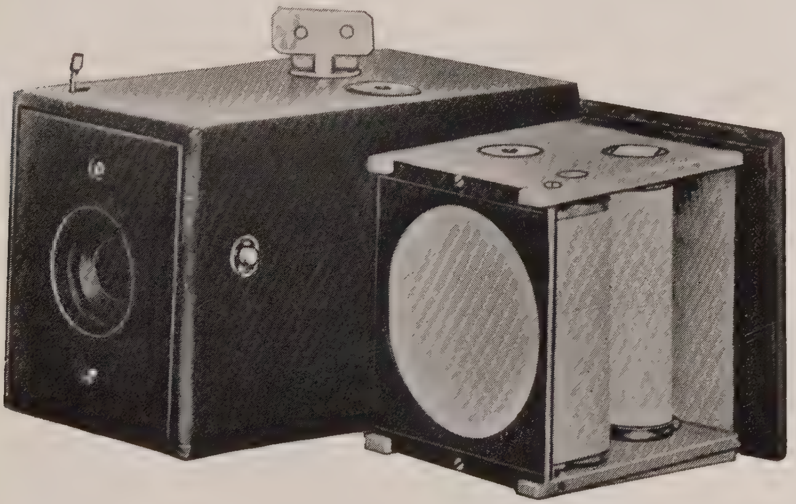


FIG. 22. First Kodak (1888).

In 1860 Bertsch of Paris designed and constructed what probably deserves to be called the first miniature camera using wet collodion plates 6 × 6 cm. (2⅜ × 2⅜ inches). Five years later, the English astronomer, C. Piazzi Smyth, constructed a camera making pictures 2.5 × 2.5 cm. (1 × 1 inches) which he used for several years. This camera was especially noteworthy in that through a special optical system an anastigmatically flat field was obtained, thus enabling the small negatives to be enlarged to 10 × 10 inches without appreciable loss of sharpness. These cameras were built by or for individuals for their own use. In 1882, however, Liesegang of Duesseldorf introduced commercially a camera called the "Liliput," making pictures 3 × 3 cm. and several other cameras making pictures about the same size were placed on the market in the next few years. These cameras were before their time and did not meet a wide reception.

In 1914, Oskar Barnack, an engineer with the optical instrument firm of Ernest Leitz of Wetzlar, Germany, designed a small camera using thirty-five millimeter motion picture film and making pictures 1 × 1½ inches (24 × 36 mm.). This camera, after having been delayed by the World War, was introduced commercially in 1924 as the *Leica.* This camera embraced a number of new and useful features and was followed within a few years by others of similar design which have formed the basis of a new and active field of photography based upon the miniature camera.

History of the Photographic Lens.—The first lens designed for photographic purposes appears to have been adapted by the Parisian optician, Chevalier, from the Fraunhofer telescope objective which has the form shown in Fig. 23. The covering power of a lens of this design is limited requiring that it be used at a rather small aperture. In 1857, the English optician Grubb patented a greatly improved lens of this type which consisted of two cemented menisci. Later Dallmeyer of London introduced a single lens which included an even wider angle and had a larger aperture. This consisted of three cemented lenses (Fig. 24). In 1888 he brought out the rectilinear landscape lens which is rectilinear despite the fact that it is a single lens.

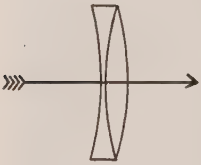


FIG. 23. Chevalier's Single Lens. Apparently the First Used for Photographic Purposes.

Single lenses were used chiefly for landscape and exterior photography. To reduce the exposure in making portraits by the Daguerreotype process, Chevalier in 1840 designed a compound portrait lens

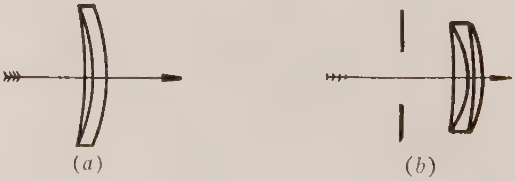
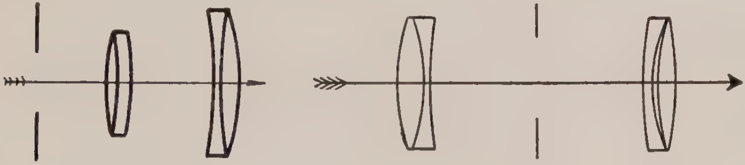


FIG. 24. Development of the Single Lens: (*a*) Grubb's Lens, (*b*) Dallmeyer's Wide Angle Landscape Lens.

which had a relative aperture of *f*/6.7. The following year, Voightlander, of Brunswick, brought out a new portrait lens designed by Professor Joseph Petzval of Vienna (Fig. 25). This lens was excellently corrected for a small angular field and had an aperture of *f*/6 which was increased almost at once to *f*/4 by Andrew Ross of London. Petzval's first objective had a chemical focus; that is the chemical and visual focus did not coincide. A decade later, he recalculated the objective and eliminated the focal difference.



(a) (b)

Fig. 25. Early Portrait Lenses: (*a*) Chevalier, (*b*) Petzval. The Speed of This Lens Contributed Materially to the Rapid Development of Photographic Portraiture.

For some years following the introduction of the Petzval lens, the efforts of opticians were directed toward the development of a lens

Fig. 26. Joseph Petzval.

which would be rectilinear, and have a larger angular field and aperture than the single lens. In 1841 Thomas Davidson designed a double lens with the diaphragm between which, however, was not a commercial success. This was the first symmetrical lens. Wolcott in the United States also patented a symmetrical lens in 1841, but his death prevented its commercial exploitation. In 1860, Harrison of New York introduced the globe lens, so called because the surfaces of the outer lenses formed a sphere. While it was free from distortion and covered a large field, the correction for spherical aberration was poor and there was some difficulty with flare. Morrison later improved on the design by making it unsymmetrical. In 1865, Steinheil of Munich introduced his periscope. This was a simple construction and covered a wide field, but was poorly corrected and had a small aperture.

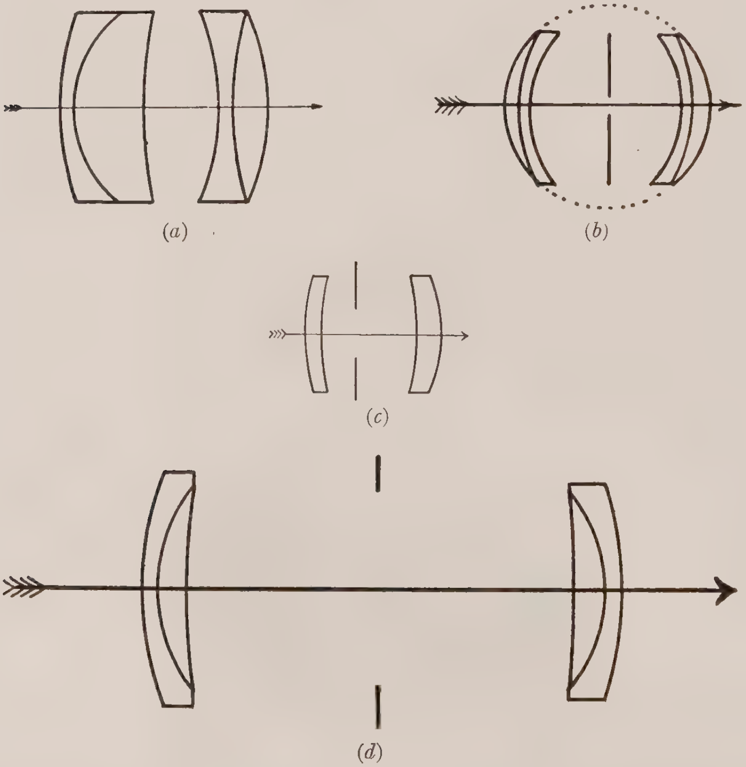


FIG. 27. Development of the Symmetrical Lens: (*a*) Ross *Doublet,* (*b*) Harrison *Globe* Lens, (*c*) Steinheil *Periscope,* (*d*) the *Aplanat* of Steinheil and *Rapid Rectlinear* of Dallmeyer.

Josef Zentmayer of Philadelphia improved the periscope by making it unsymmetrical, the back lens having the shorter focal length.

Thomas Ross of London patented an improved doublet in 1865 which was moderately successful despite the rather small aperture. All of these lenses were eclipsed by the introduction of the *aplanat* of Steinheil (Munich) and the *rapid rectilinear* of Dallmeyer (London) in 1866.

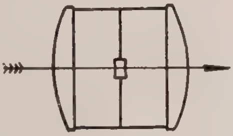


FIG. 28. Sutton's Triplet Lens.

The principle utilized in the aplanat and the rapid rectilinear was discovered independently by Steinheil and Dallmeyer and involved the use of two flint glasses of more nearly the same refractive index than the flint and crown glasses used in the earlier double lenses. This greatly reduced astigmatism and improved the correction for the other aberrations. It did not, however, permit the simultaneous removal of astigmatism and curvature of field. This was accomplished only after the introduction of the newer varieties of glass by the Jena Glass Works had made possible the *anastigmat*. The aplanat, or rapid rectilinear, as it is commonly termed in English speaking countries, represented a signal advance in photographic optics and is one of the three lenses discussed thus far to survive; the others are the Petzval portrait lens and the single lens of Grubb.

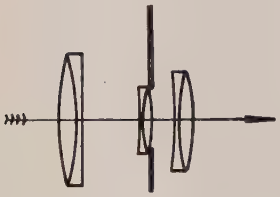


FIG. 29. Dallmeyer's Triple Achromatic Lens.

Thomas Ross apparently made the first triplet construction of three single lenses for Fox-Talbot in 1841, and in 1860 Thomas Sutton took out a patent for a triplet (Fig. 28). The first triplet design to be placed on the market, however, was the Dallmeyer triplet (Fig. 29) which appeared the same year and was made for several years. The most important triplet construction is that of H. D. Taylor which, as an anastigmat, will be discussed under that heading.

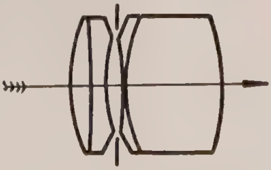


FIG. 30. The *Antiplanat* of Steinheil.

The *Antiplanat* (Fig. 30), introduced by Steinheil in 1879, may be regarded as the immediate predecessor of the anastigmat. In this lens the symmetrical arrangement was departed from. The element in front of the diaphragm is positive and that in the rear is negative in effect, although only to a slight extent. Thus by compensating for the errors of one element by errors of the opposite character in the element on the other side of the diaphragm, Steinheil was able to improve the correction for astigmatism and at a larger aperture than had been possible with the aplanat. The Antiplanat, despite the great originality displayed in its design, was soon superseded by the anastigmats which made their appearance almost exactly ten years later (1890).

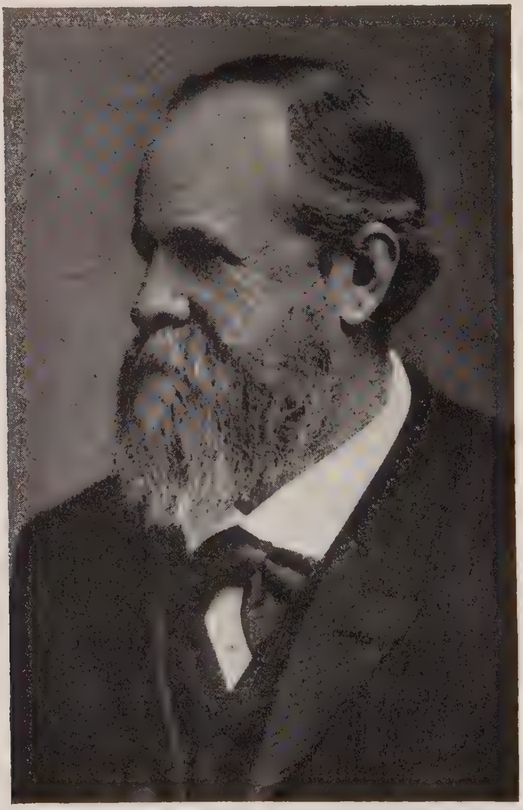


Fig. 31. Adolph Steinheil.

The first lens in which the new Jena glasses were used to produce an objective free from astigmatism and with a flat field was calculated by Schroeder and introduced by Ross Ltd., of London, in 1888 as the *Concentric* (Fig. 32). It was not well corrected spherically, requiring a small stop to obtain good definition, and was soon withdrawn. The first objective in which adequate correction for spherical aberration and astigmatism were combined with a flat field was patented by Paul Rudolph, of Jena, and introduced in 1890 by Carl Zeiss as the *Protar*.

This was developed through the addition of air spaces first into the *Unar* (1897) and then into the *Tessar* (1902). This last has been one of the most popular lenses ever designed and has been copied all over the world. Rudolph designed also a three and a four element symmetrical objective (Fig. 33) either half of which might be used alone to obtain lenses of different focal lengths. The three-lens design was designed and patented independently by von Hoegh of Goerz in Berlin and issued commercially as the *Dagor* (1892). The four-lens design was placed on the market by Rudolph's own firm Carl Zeiss of Jena as the *Protar* (1895). Similar three and four lens designs were later placed on the market

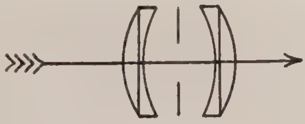


Fig. 32. The *Concentric* of Ross.

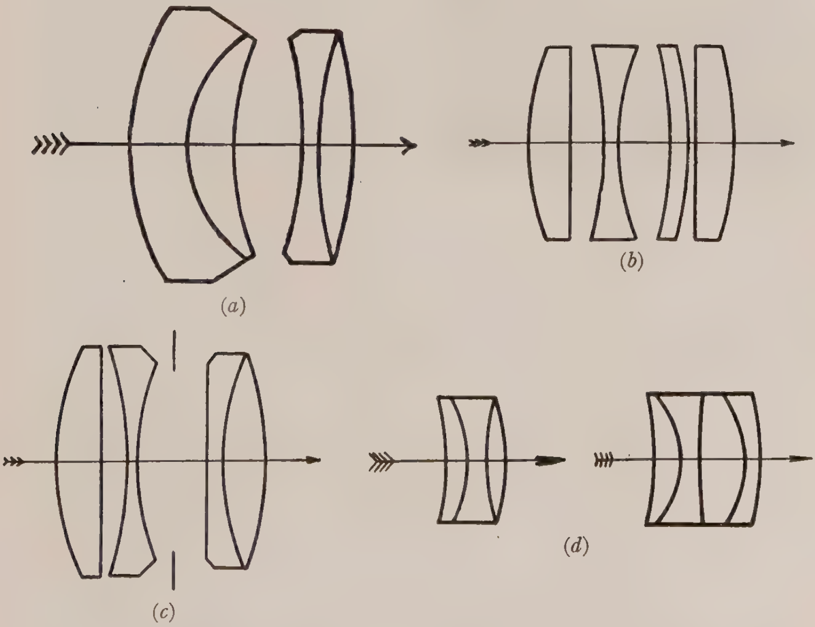


Fig. 33. Four Early Anastigmatic Lens Designs by Paul Rudolph: (*a*) Early *Protar*, (*b*) the *Unar*, (*c*) the *Tessar*, (*d*) Three- and Four-glass Symmetrical Objectives.

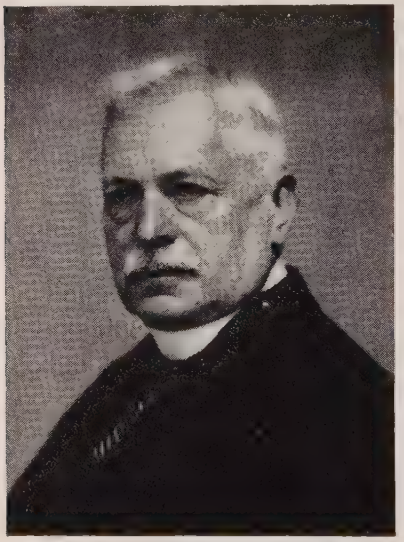


FIG. 34. Paul Rudolph.

by Voightlander of Brunswick (*Collinear*), Ross of London (*Combinable*) and many others. In 1893, H. D. Taylor of England designed an anastigmatic objective of large aperture consisting of only three simple lenses (Fig. 35) which became known as the Cooke triplet after the firm of T. Cooke by whom Taylor was employed. This brilliant achievement was likewise widely copied by other manufacturers. From it were developed the *Heliar* of Harting, the *Aviar* of Warmisham, the *Aldis* of Aldis Brothers, and many others.

In 1897 Rudolph designed a large aperture anastigmatic objective based upon the Gauss telescope objective which was introduced by Carl Zeiss of Jena as the *Planar* (Fig. 36). This design likewise has been widely copied especially for short focus large aperture objectives for miniature cameras and cinematography.

The earliest photographic application of a rear negative element to a

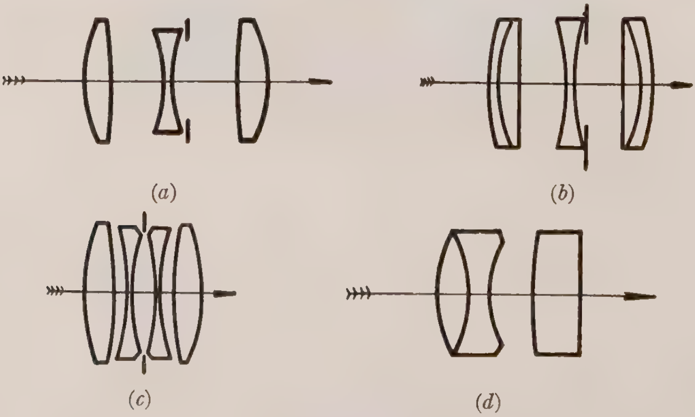


FIG. 35. (*a*) The *Cooke* Lens of H. D. Taylor, (*b*) *Heliar,* (*c*) *Aviar* and (*d*) *Aldis.*

photographic objective in order to form a telephoto objective appears to be due to J. Porro in 1851. The first telephoto objective to be placed on the market was the *Orthoscope,* designed by Petzval in 1840 or 1841, although not placed on the market until 1857. It consisted of two elements (Fig. 37) separated by the diaphragm. The front element is similar to that of the Petzval portrait lens and is positive; the rear element is negative and enlarges the image formed by the front lens. Little or no attention seems to have been paid to this characteristic of the Orthoscope lens and it disappeared from the market with the advent of the aplanat and the telephoto lens was really developed by Steinheil, of Munich, and Dallmeyer, of London. The latter took out a British patent in 1890 for a compound telephoto objective which consisted of a well corrected photographic lens and a back negative element composed of two achromatic lenses; as the distance between the two was variable a wide range of magnification was possible.

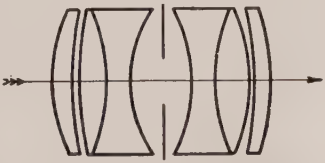


FIG. 36. The *Planar* of Paul Rudolph.

It was not until 1905 that the first of the modern fixed magnification telephoto objectives was introduced; the *Bis-Telar* of Emil Busch. This was designed by K. Martin and had a relative aperture of $f/9$ and a magnification of 2.

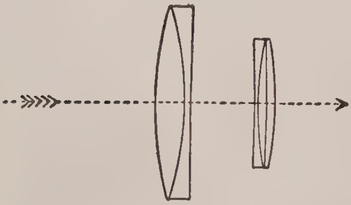


FIG. 37. The *Orthoscope* of Petzval.

The following year Zeiss brought out the *Magnar* which had a relative aperture of $f/10$ and a magnification of 3. Similar objectives but with improved astigmatic correction and of larger aperture were designed in 1912 by Hasselkus, of Ross Ltd., and two years later by Lan Davis, of Dallmeyer Ltd., both of London. The first was introduced as the *Telecentric* in two series, one with a relative aperture of $f/5.4$ and the other $f/6.8$. The second was placed on the market as the *Large Adon* and had an aperture of $f/4.5$.

Fixed magnification telephoto objectives introduced since 1914 will be discussed in chapter on the Photographic Objective.

History of Shutters.—In the early days of photography, there was little need for a shutter as the lengthy exposures required by the negative materials then available could be made readily by means of a cap over the lens. The first shutter may have been the one used by Fizeau and Foucalt in 1845 to make Daguerreotypes of the sun. This consisted of an opaque panel with an aperture the size of the lens sliding in two tracks which permitted it to fall by gravity so that the aperture passed in front of the lens and exposed the sensitive materials. This type of shutter was popular for several years and is known as the *"drop shutter"* or *guillotine* from its similarity to the instrument of that name. An early shutter of this type is shown in Fig. 38.

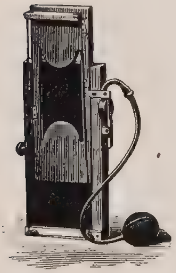


Fig. 38. Guillotine or Drop Shutter.

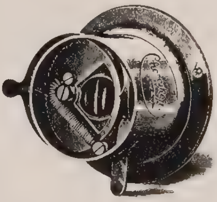


Fig. 39. Rotary Shutter.

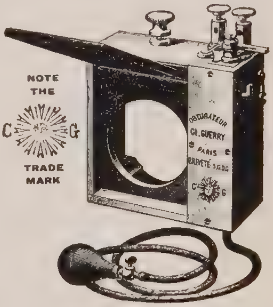


Fig. 40. Flap Shutter.

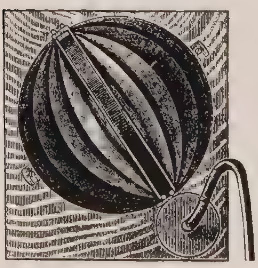


Fig. 41. Bellows Shutter.

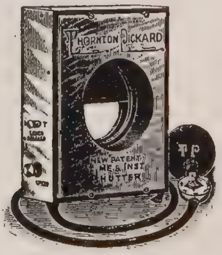


Fig. 42. Roller Blind Shutter.

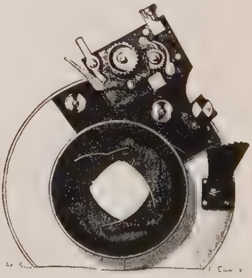


Fig. 43. Early Between-the-lens Shutter.

Rotary shutters consisting of a rotating circular screen with an aperture which is caused to pass in front of the lens by a spring mechanism, were developed about 1860. An early shutter of this type is shown in Fig. 39. This type of shutter is still employed on many box cameras. Fig. 40 illustrates a simple *flap* shutter. Early models were operated by strings, later a spring was used to keep the flap in position over the lens and pneumatic action employed to raise the flap for the exposure. This type of shutter is not suitable for very short exposures and was intended chiefly for studio work. In modified forms, it is still used for portrait work. Cadett patented a shutter of this type, in which the flap was a bellows (Fig. 41).

The *roller-blind* shutter consists of a flexible opaque blind or curtain with apertures. This blind unwinds from one roller to another under tension, the exposure being made when the aperture in the curtain passes the lens. This type of shutter seems to have originated about 1855 but did not become popular until much later. A typical roller-blind shutter, popular at the turn of the century, is shown in Fig. 42. A modification of the roller-blind shutter in which the curtain is placed directly in front of the film or plate is known as the focal-plane shutter. The focal-plane shutter was patented by Anschutz in 1888 and placed on the market by Goerz of Berlin in 1890.

An early two-blade shutter, the forerunner of modern between-the-lens shutters, is shown in Fig. 43. This was patented in 1882. Dallmeyer and Beauchamp in London and Bausch and Lomb of Rochester, New York, contributed greatly to the development of precision between-the-lens shutters. The work of Deckel in Munich, resulting first in the pneumatically controlled *Compound* (1902), and the gear-controlled *Compur* (1912), is worthy of mention.

Color Photography.—Methods of producing photographs in natural colors may be divided into two classes, (1) *direct,* depending upon the bleaching of light-sensitive dyes or light interference and (2) *indirect.*

Direct Processes of Color Photography.—Seebeck in 1810 found that silver chloride when exposed to the rays of light partook slightly of the colors themselves and Edmond Becquerel in 1844 reproduced more or less perfectly the seven principal colors of the spectrum on a Daguerreotype plate. The colors were lost, however, when the plate was fixed. Similar processes were described by Herschel, Niepce de Saint Victor and Robert Hunt.

In 1897 Lippman of Paris described a process of natural color photography based upon the principle of light interference. A grainless albumin film was exposed in front of a mirror, formed by a bath of liquid mercury, developed and fixed in a weak solution of cyanide resulting in a brilliantly colored image when viewed by light reflected from a mirror. The results, however, cannot be duplicated, the process is slow and tedious, and natural colors are not well reproduced, hence, the process remains no more than an interesting demonstration.

Indirect Processes of Natural Color Photography.—Promising as such processes of natural color photography may appear theoretically, it is with indirect methods involving the separate registration of the three fundamental color sensations and their subsequent recombination that the greatest progress has been made.

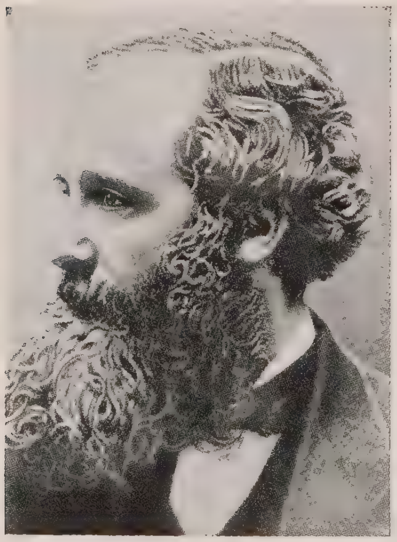


Fig. 44. Clerk-Maxwell, Renowned English Physicist Who Enunciated the Electromagnetic Theory of Radiation.

The first to apply such methods was James Clerk-Maxwell, of the Royal Institution in London, who in 1861 took three photographs, one through a red solution acting as a color filter, one through a green solution, and a third through blue-violet. From these negatives he had lantern slides made which he projected on top of one another by means of three lanterns; each one projecting its slide through the solution which had been used in making the original negative. The result was not wholly successful (1) because the wet-collodion process was almost insensitive to green and red, and (2) because the solutions employed did not have the proper spectral transmissions.

In 1862, Louis Ducos du Hauron deposited with the French Academy of Sciences a paper on processes of color photography which, however, was not presented to the Society nor was it published until 1897. In the meanwhile, he published (1869) *Les Coleurs en Photographie, Solution du Probleme* in which he described (1) a tri-color camera for making three-color negatives with one exposure, (2) combining positives on glass from the three negatives in a viewing device similar to the camera to produce an image in colors, (3) printing from three-color negatives by the carbon process to produce a print in colors, and (4) the screen plate process.

In 1895, he patented a tripack, the three plates being placed together with their respective filters in between, thus enabling the three negatives to be made with one exposure in an ordinary camera.

While all subsequent progress in color photography has been along these lines, du Hauron was unable to perfect any of these methods owing to the limited sensitivity of the negative materials then available and to his limited financial resources.

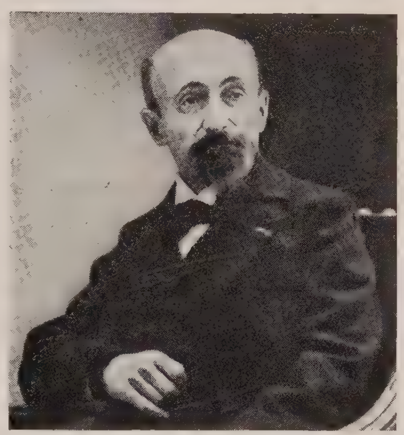


FIG. 45. Ducos duHauron, Whose Fertile Imagination Visualized Most of the Processes of Three Color Photography, Later Developed Practically by Others.

Three-color cameras and viewing instruments were brought to a high degree of perfection by F. E. Ives of Philadelphia, who during his long association with color photography added greatly to our store of knowledge of all processes (except the screen-plate). Space does not permit an extended treatment of the history of tri-color cameras nor viewing instruments (photo-chromoscopes). An excellent survey of the various types is available in the *History of Three-Color Photography* by E. J. Wall (Boston 1925).

Subtractive Printing Processes.—Since du Hauron first suggested the carbon process as a means of making the three-color images required by subtractive printing processes, many other methods have been exploited. These include the production of dye images (1) by mordanting methods, (2) differentially hardened gelatin, (3) gelatin relief images, (4) imbibition processes based upon the transference of dyes from gelatin printing plates produced by methods 2 or 3, (5) toning of silver images with metallic compounds, (6) pigment processes such as carbon, gum-bichromate and, more recently, three-color carbro, (7) developers producing color images and (8) processes employing diazo dyes.

Screen Plate Processes.—In just the same way that a painter may secure a certain color by the juxtaposition of dabs of pigment of two colors which when viewed at a distance merge to form a single color, so it is possible to secure on a single plate all three-color-sensation records by employing in place of the usual solid color filter a multi-color screen composed of a large number of small color screens evenly distributed and so small as to be practically invisible. The multi-color screen was the conception of Louis Ducos du Hauron in 1868.

Screen plates were produced by Joly (1894), McDonough of Chicago (1896), Brasseur of London (1896), Powrie of Chicago (1905), Smith of London (1906), Krayn (1904), Dufay (1908), and by Finlay of London (1906), but the first commercially successful screen plate process of color photography was the Lumière Autochrom patented in 1903 and placed on the market in 1907.[22]

The lenticular screen in which the film is embossed so as to form minute lenses imaging a three-banded filter placed over the camera lens was suggested by Liesegang of Elberfeld, Germany in 1896. The process was developed practically and patented by Berthion of Paris in 1908. In 1928, the rights to the Berthion patents were acquired by the Eastman Kodak Company and utilized in a process of amateur cinematography known as *Kodacolor,* since replaced by *Kodachrome.*

Mention was made in a preceding paragraph of the possibility, envisaged by duHauron, of making three color negatives by means of a tripack in which three emulsions are exposed together in contact with one another, each emulsion recording only one of the three primary color sensations, a result obtained by appropriate color sensitizing and the use of dyed gelatin layers which serve as filters. DuHauron visualized such a tripack as consisting of three separate films but it is clear that the three emulsions may also be coated on top of one another on a single support to form what is termed an *integral* tripack or *monopack*. J. H. Smith produced an integral bipack (two emulsions) experimentally in 1903, and Schnizel in 1905, and Sforza in 1909 proposed integral tripack processes. Difficulties were experienced, however, not only in the manufacture of the tripack but in converting the three negative images into positive images of the proper colors and it remained for Mannes and Godowsky in the Kodak Research Laboratories to develop a commercially practical integral tripack process for the production of transparencies in color which was introduced as *Kodachrome* by the Eastman Kodak Company in 1935.

An integral tripack negative material and a corresponding positive material for producing prints in color was introduced by the Eastman Kodak Company as *Kodacolor* in 1942.

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[22] The most convenient source of reference is Wall, *History of Three Color Photography.* American Photographic Publishing Co. (Boston 1924).

Gasparcolor, a process developed by Dr. Bela Gaspar, employs a tripack in which two of the emulsion layers are on one side of the support and the third on the opposite side. At this writing it is employed commercially only as a means of positive printing for motion pictures in color.

Agfacolor, an integral tripack process for color transparencies, was developed in the Agfa laboratories in Germany and introduced commercially in Europe in 1936. It has not been placed on the market in the United States of America.

Photographic Periodicals.—The first periodical[23] devoted exclusively to photography seems to have been the *Daguerreian Journal* which began publication in New York in November 1850. After the introduction of the wet collodion process, the practice of photography became more widespread and periodicals were established to serve the new field. Many of the journals established in these years exist today, as for example, the *Liverpool Photographic Journal,* established in 1854, and since 1856, the *British Journal of Photography;* the *Journal of the Photographic Society of London* which began publication in March 1853 and since 1859 as the *Photographic Journal,* the organ of the Royal Photographic Society of Great Britain. In France, the first important, if not actually the first photographic publication, was the *Bulletin de la Société française de Photographie,* established at Paris in 1855. In Belgium, the *Bulletin Belge de la Photographie* (Brussels 1861); in Germany, the *Photographisches Journal* (Prague 1854), *Photographische Archiv* (Duesseldorf 1860) and *Photographische Korrespondenz* (Vienna 1864) were among the earliest.

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[23] The first real journal of photography in the U. S., however, was the *Philadelphia Photographer,* established by Edward L. Wilson in 1864. In 1867 it absorbed the *American Journal of Photography* and *Humphrey's Journal.* Later, it became *Wilson's Photographic Magazine,* then the *Photographic Journal of America* and finally in 1924, was merged with the *Camera* (Philadelphia).

CHAPTER II

PHOTOGRAPHIC OPTICS

Introduction.—Light is that form of radiant energy which is capable of affecting our sense of sight. The exact nature of light has been a subject of much conjecture among physicists and philosophers for many centuries. One can conceive of energy being transferred from one place to another in two ways only, one of these being by means of the passage of material units from one position to a second (bullets, for example), the other being by means of the passage of a wave motion from place to place (waves in the ocean). Most ancients considered that a beam of light consisted of streams of sub-microscopic particles which radiated uniformly in all directions from the light source. This corpuscular theory of light, supported by Newton among others, held full sway in the minds of most physicists until Thomas Young, in the year 1800, published a paper in the *Philosophical Transactions of the Royal Society* entitled, "Outline of Experiments and Inquiries Respecting Light and Sound." In this and other papers Young, supported by the work of Fresnel, established the wave theory of light put forward earlier by Huygens (1629–1695). Young showed both by experimentation and mathematical reasoning that light energy must be of an undulatory or wave nature if such phenomena as diffraction and interference are to be explained in a rational manner. The work of such scientists as Foucault in measuring the velocity of light in different media and Fraunhofer in establishing the wave length of various dark lines in the solar spectrum culminated in the mathematical development by Maxwell and experimental verification by Hertz of the electromagnetic theory of radiation, including light.

Electromagnetic Theory of Radiation.—Maxwell's comprehensive theory (1870) predicted the existence of radio waves which were later discovered by Hertz. This elaborate theory of wave motion seemed to cover and explain all optical phenomena and physicists in general considered that an elaboration of known facts was all that remained to be done. Light and similar forms of radiation were presumed to be transmitted as waves through the hypothetical all pervading ether. Such radiations are characterized by moving electrical and magnetic forces.

The first determination of the velocity of electromagnetic waves was obtained from Roemer's observations in 1675 although at that time the value was ascribed only to light. The velocity of light is one of the most accurately known physical constants. Many experiments have been made from the time of Galileo up to the present to determine this important velocity. Roemer's value for the velocity of light was obtained from a study of the revolution periods of a satellite of the planet Jupiter as observed from various positions of the earth traveling in its orbit around the sun. Roemer's value for the velocity of light in free space was 3.0×10^{10} centimeters per second, a figure in remarkably close agreement with the latest values obtained from Michelson's terrestrial experiments (2.99796×10^{10} centimeters per second). The velocity of light in other media varies with the nature of the medium and the frequency of the light. The average value for glass, for example, is about two-thirds of its velocity in a vacuum.

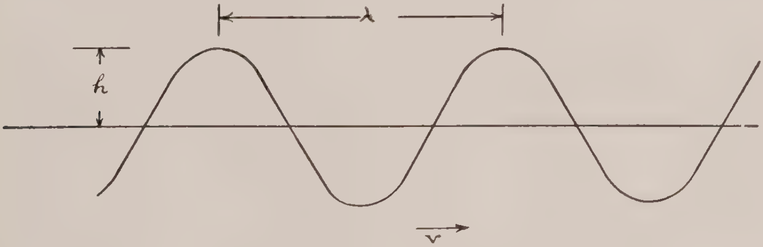

FIG. 46. Wave Motion.

λ = One wave-length mμ.
V = Velocity of travel of the wave, cm./sec.
h = Amplitude of the wave, mμ.
T = period, or the time required for one wave to pass a fixed point, sec. ($T = \lambda/V$).
f = frequency = $1/T = V/\lambda$.

Since electromagnetic radiations are transmitted in the form of a wave motion, there must be connected with any given radiation a specific wave length. Fig. 46 represents the simplest form of wave motion, namely, a sinusoidal motion of particles forming a transverse wave. This diagram is introduced primarily to aid in the definition of terms which are commonly used when describing wave phenomena. The distance between corresponding positions of two adjacent waves represents one wave length, the symbol for which is λ. Let V be the velocity of travel of the wave and T the time required for one wave to pass a fixed point. Then $\lambda = VT$. The quantity T is usually referred to as the period, while its reciprocal, $1/T$, is known as the frequency, the symbol for which is f. Expressing λ as a function of f, we have $\lambda\ (T/f)$.

The various types of electromagnetic waves are shown in the following table:

Type of Radiation	*Wave Length (average)*	*Detection*
Radio	10^{11}Å	Electrical receivers
Infra-red	10^{6}Å	Bolometer; Photographic emulsion
Visible Light	6000Å	Eye; Photographic emulsion
Ultra-violet	1000Å	Fluorescence; silver halides
X-rays	1.0Å	Ionization; silver halides
-rays	.05Å	Ionization; silver halides
Cosmic-rays	.0001Å	Ionization; silver halides

The tremendous extent of the electromagnetic spectrum is illustrated in Fig. 47. The characteristic difference between the various radiations is their wave length. For visible light the wave length region is very short and the frequency of green light, for example, is $6 \cdot 10^{14}$ or six hundred thousand billion vibrations per second. Radiation of a

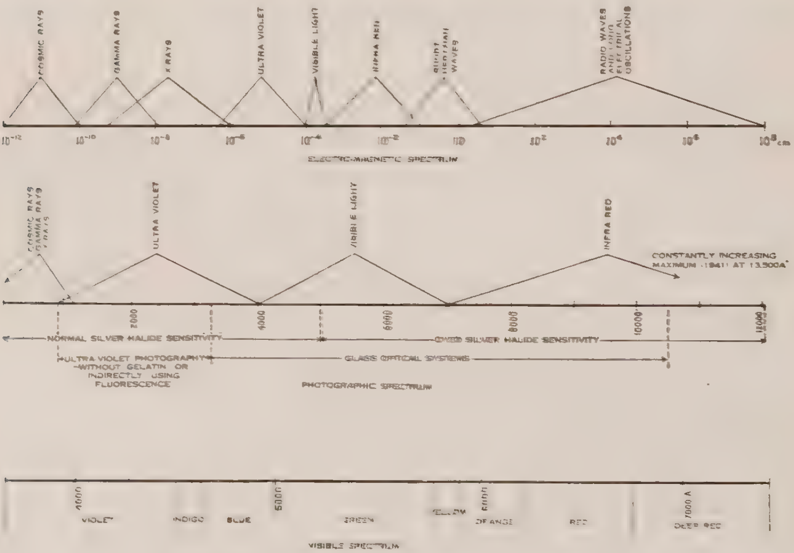

Fig. 47. The Electromagnetic Spectrum.

single wave length is called monochromatic[1]; of a complex nature, heterochromatic. Because of the extreme shortness of the wave lengths of light, the customary units of inches and centimeters are usually replaced by more convenient units. These units are:

Micron (μ) = 1/10,000 cm. = 10^{-4} cm.
Millimicron (mμ) = 1/10,000,000 cm. = 10^{-7} cm.
Angstrom unit (Å) = 1/100,000,000 cm. = 10^{-8} cm.

Radiation within the region from 400 to 700 mμ is visible as light. The radiations within the region excite the following color sensations:

Violet	400–450 mμ
Indigo	450–460 mμ
Blue	460–500 mμ
Green	500–580 mμ
Yellow	580–590 mμ
Orange	590–620 mμ
Red	620–700 mμ

Discontinuous Radiation.—At the turn of the last century when physicists considered that the electromagnetic theory was the final answer to their investigations into the nature of radiation, new experimental facts were discovered that could not be explained on the established classical theory. The facts of black body radiation[2] which had defied explanation on the basis of waves were successfully explained by Planck in 1900. When an object is heated up to incandescence, the quantity of energy radiated constantly increases and the character of the radiation is altered. The wave length of maximum radiation is shifted toward the shorter wave lengths with any increase in the temperature of the radiating source. This alteration in the character of the emitted radiation leads to a relatively greater increase in radiated energy at the higher frequencies as compared with the lower frequencies whenever the total radiation is increased due to a rise in the temperature of the source of radiation.

The total radiation emitted by a perfect black body varies as the fourth power of the temperature (Stefan's Law) and the wave length of maximum radiation is given by Wien's Law $\lambda_{(\text{max.})} = CT$. The curves in Fig. 48 were obtained experimentally but a theoretical equation [3] which agrees with the observations was derived by Planck using the hypothesis that radiation is discontinuous and is only emitted in definite quanta or multiples thereof. There is thus a revival of the idea that radiation is discontinuous. Other experimental evidence difficult to explain on the wave theory is the photo-electric effect. Hertz observed that a spark passed more readily between two electrodes when they were strongly illuminated and other observers noted that various metal plates, when illuminated, emitted electrons. These observations could not be explained on the classical wave theory but were readily understood when considered in conjunction with the quantum theory.

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[1] Because of the practical difficulties in obtaining truly monochromatic radiation, a very limited band of wave lengths is often termed monochromatic.

[2] A black body is one that absorbs all the incident radiation and also one that radiates more energy than any other body at the same temperature.

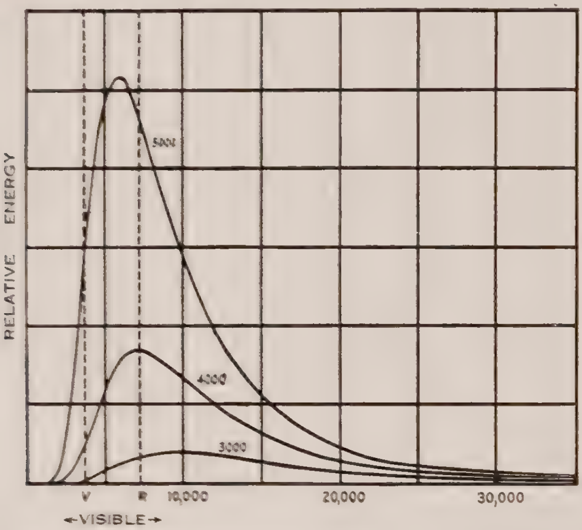

FIG. 48. Relative Energy Distribution Plotted Against Wave Length for Three Temperatures.

Radiation, including light, is now regarded as being composed of bundles of energy in the form of quanta which have definite wave properties. Hence, light is considered as possessing undulatory as well as corpuscular characteristics. Perhaps the nature of light may be best expressed as being undulatory and or corpuscular, the nature depending entirely on the physical phenomena which are to be explained. The wave theory is usually employed when explaining such phenomena as reflection, refraction, interference, and polarization; and the quantum theory for such phenomena as photo-electricity and recently observed effects in the field of X-rays and similar radiations.

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[3] Planck's theoretical equation $E_\lambda = \dfrac{C_1\lambda^{-5}}{\epsilon^{C_2/\lambda T} - 1}$ relates the energy emitted with the temperature of the source. For a discussion, see any text of Modern Physics

Reflection and Refraction of Light.—A ray of light traveling in a homogeneous medium forms a straight-line path. However, when a light ray is incident upon a surface separating two different media, the path is in general broken at that point. In fact, the ray is divided into two portions, one of which proceeds into the second medium in a different direction, while the other is reflected back into the first medium.

Should a normal be erected to the boundary surface at the point where it receives the incident ray, the angles which the incident, refracted and reflected rays make with this normal, all lie in the same plane. Further *the incident and reflected rays make equal angles with the normal.* See Fig. 49. The angle of the refracted ray with the normal, however, is smaller than either the incident or reflected angle, provided the second medium is more dense than the first.

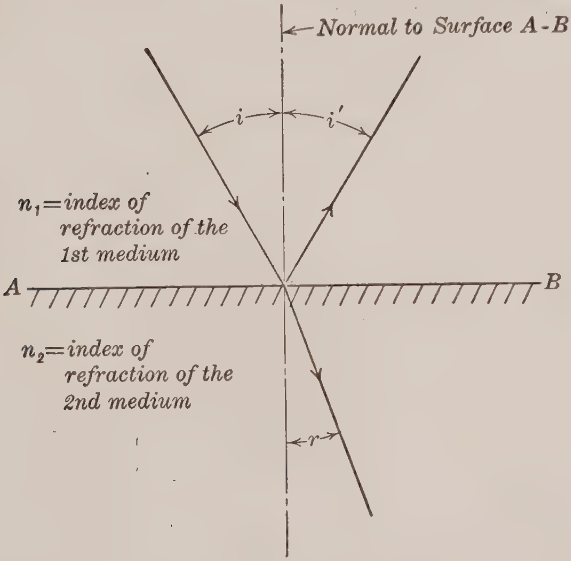
Normal to Surface A-B
i
i'
n_1=index of refraction of the 1st medium
A
B
n_2=index of refraction of the 2nd medium
r

FIG. 49

i = angle which incident ray makes with normal to surface A–B
i' = angle which reflected ray makes with the normal to surface A–B
r = angle which refracted ray makes with the normal to surface A–B

The Law of Reflection.—The angle of incidence is equal to the angle of reflection and both lie in the same plane.

The Law of Refraction.—The sine of the angle of incidence divided by the sine of the angle of refraction equals the index of refraction of the second media with respect to the first. In mathematical language, this may be expressed as:

$$n = \frac{\text{sine of the angle of incidence}}{\text{sine of the angle of refraction}} = \frac{\sin i}{\sin r}$$

where n is known as the index of refraction of the second media with respect to the first.

In terms of the velocity of light, the index of refraction of any particular substance may be expressed as the ratio between the velocity of light in vacuum to that of the velocity of light in the medium being considered. Therefore, $n = V/V'$ where V represents the velocity of light in vacuum and V' the velocity of light in the medium being considered. The refractive indices of several common optical materials are given in the following table.

Index of Refraction of Optical Glass
(relative to air)

Type of Glass	*Wave Length, millimicrons*						
	400	450	500	550	600	650	700
Silicate Flint........	1.6528	1.6391	1.6302	1.6240	1.6193	1.6157	1.6129
Telescope Flint......	1.5393	1.5320	1.5270	1.5233	1.5206	1.5184	1.5166
" Crown.....	1.5406	1.5346	1.5304	1.5273	1.5249	1.5231	1.5216
Borate Flint.........	1.5938	1.5858	1.5802	1.5761	1.5730	1.5705	1.5685
Dense Crown........	1.5917	1.5855	1.5812	1.5780	1.5755	1.5736	1.5720
Light Crown.........	1.5232	1.5174	1.5134	1.5104	1.5082	1.5064	1.5049
Quartz..............	1.5577	1.5519	1.5488	1.5460	1.5438	1.5421	1.5407
Fused Quartz........	1.4700	1.4656	1.4624	1.4600	1.4581	1.4566	1.4553

The relative intensity of the reflected and refracted rays depends upon the character of the boundary surface between the two media. In general, a polished metallic surface reflects the larger proportion of light. The refracted portion is absorbed in an exponential fashion as it proceeds into the second medium.

Wave Front.—An important concept to understand in connection with the wave theory of light is the so called "*wave front.*" The motion of a light wave in three-dimensional space may be likened unto the motion of a surface in which the phase of disturbance is everywhere identical. A surface of this character represents a so-called wave front. To illustrate this further, let us consider *S,* Fig. 50, as a point source of light located in a homogeneous medium. Under such conditions, the velocity of propagation will be equal at all points and in all directions, and the wave front will emanate from the source as spheres of ever-increasing radii. At any particular instant, the disturbance may be visualized as a series of concentric spheres the loci of which are the source of light.

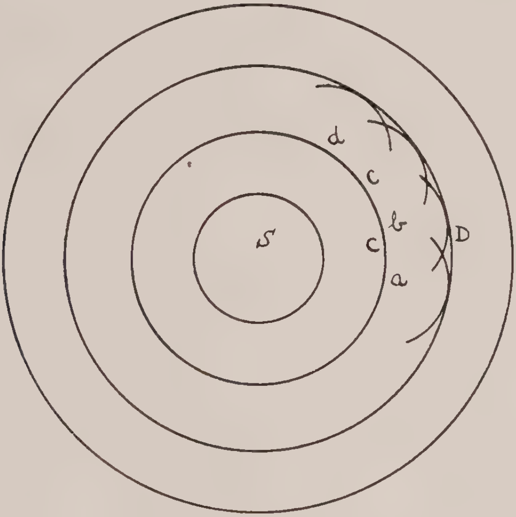

Fig. 50. Wave Front.

About the middle of the seventeenth century, Huygens pointed out that successive wave fronts need not of necessity be considered as having originated from the light source. In other words, the wave front may be considered as having originated from the disturbance on wave front *C* instead of from the Source *S*, in which case each point on the wave front *C* would act as a center of disturbance from which secondary spherical waves emanate. Therefore, the wave front *D* describes the envelope of spheres of equal radii whose centers lie on surface *C*. Huygens' wave front method offers a most direct approach to the facts of image formation and is consequently an invaluable aid of geometrical optics.

Polarized Light.—When one oscillates the end of a stretched rope with a periodic up-and-down motion, a set of transverse waves pass along the rope. A wave train of this type is known as a *plane-polarized* train of waves. If instead of moving the hand up and down a circular motion is imparted to it, a set of *circularly-polarized* waves is sent out along the rope. And likewise, if an elliptical motion is given to the hand, the waves which travel along the rope are said to be *elliptically-polarized.* Ordinary or natural light is considered to be composed of beams of plane-polarized light where all azimuths are represented.

It is possible by various polarizing devices to change a natural light wave in such a fashion that only one direction of vibration is left, that is, it becomes plane-polarized. Natural light passing through a crystal of Iceland spar becomes plane-polarized. Ordinary unpolarized light which is specularly reflected at an angle of 32 to 37 degrees from any non-metallic surface is strongly polarized by the act of reflection. Light from a clear blue sky arising at right angles to the sun's rays is also strongly polarized.

Absorption.—When light passes through a material, some of its energy is lost by surface reflection and some by absorption within the material itself. Fig. 51 shows a beam of intensity I_0, incident upon the surface AA of a piece of glass of thickness x. At the first surface approximately 4% of the incident light is lost by reflection in beam Ir_1. Of the remaining 96% a certain amount is lost by absorption (beam Ia), the magnitude of this loss depending upon the character of the glass as well as its thickness. At the second surface (BB) another reflection loss occurs so that the final beam Ix has an intensity equal to $I_o - (I_{r_1} + I_a + I_{r_2})$. Therefore, the fraction of the incident light which is actually transmitted is represented by I_x/I_o—this quantity being known as the *transparency* of the material. The reciprocal of the transparency is known as the *opacity,* that is $O = 1/T$. The so-called *density* of the material is defined as the natural logarithm of the opacity:

$$D = \log_{10} O = \log_{10} \frac{1}{T}.$$

In general, the absorption of a material depends upon its thickness in an exponential fashion in accordance with Bouguer's law, which may be stated as follows: $I = I_o t^x$ where x is the thickness of the material and t the transmission for a unit thickness. This law may also be written $I = I_o e^{-ax}$ where a is the so-called absorption coefficient of the material.

The amount of light which a material absorbs is also a function of the wave length of the light. Therefore, absorption is said to be a selective phenomenon. Materials which are non-selective are of a neutral gray color.

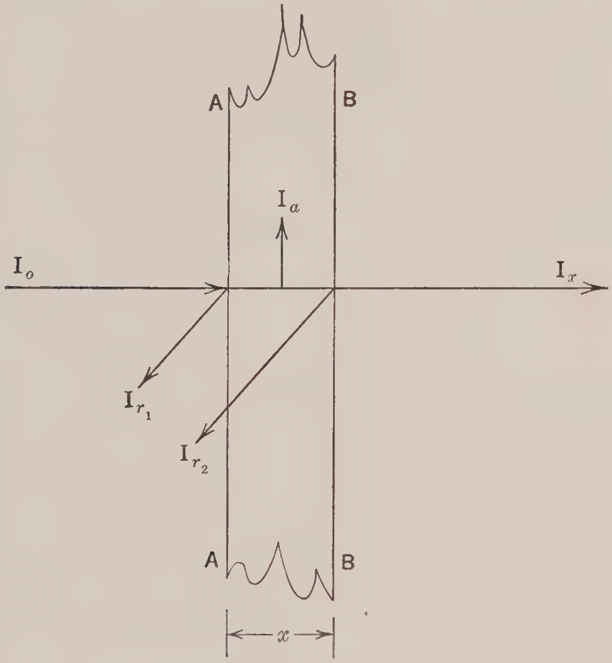

Fig. 51. Absorption.

The Reflection of Light by a Spherical Surface.—Fig. 52 shows a concave spherical reflection surface whose center is at V. The line OV is termed the axis of the mirror and the point V its vertex. The location of the image O' of the axial point object O may be determined in accordance with the following formula:

$$\frac{1}{u}+\frac{1}{v}=\frac{1}{f},$$

where u equals the object distance OV, v the image distance $O'V$, and f the focal length of the mirror whose value equals $R/2$.[4]

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[4] In order to avoid ambiguity, it becomes necessary to adopt a sign convention to insure consistency in the uses of formulae relating to optical imagery. Since no convention is strictly universal, we shall select that used by Messrs. Hardy and Perrin in their recent text entitled "Principles of Optics." To quote:

If one wishes to image a light source at infinity, that is, to produce parallel light by means of a concave mirror, it becomes necessary to place the light source at the focus of the mirror. Under these conditions, all the rays which fall upon the mirror will be reflected parallel to the axis. It becomes obvious that it is advantageous to make the mirror as large as possible in order to receive a high percentage of the rays from the source and hence concentrate more light upon distant objects. The previous formula is only a good first approximation and it will be found by experimentation that as the mirror is made larger the imagery becomes more and more inaccurate and parallelism of the projected rays less perfect. If instead of using a spherical mirror, a parabolic shape is resorted to and the source placed at its focus, it will be found that better results are obtained, since the geometrical properties of a parabolic surface are such that all rays are projected in a parallel beam no matter how large a portion of the surface is utilized.

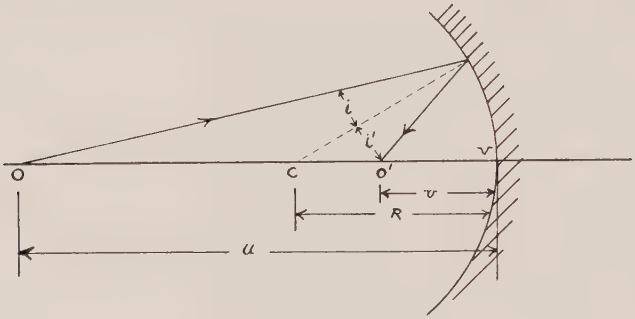

FIG. 52. Reflection Spherical Mirror.

"1. Draw all figures with the light incident on the reflecting or refracting surface from the left.

"2. Consider the object distance u positive when the object lies at the left of the vertex V.

"3. Consider the image distance v positive when the image lies at the right of the vertex V.

"4. Consider the radius of curvature R positive when the center of curvature lies at the right of the vertex.

"5. Consider slope angles positive when the axis must be rotated counterclockwise through less than $\pi/2$ to bring it into coincidence with the ray.

"6. Consider angles of incidence and refraction positive when the radius of curvature must be rotated counterclockwise through less than $\pi/2$ to bring it into coincidence with the ray.

"7. Consider distances normal to the axis positive when measured upward."

Fig. 53 shows an exaggerated example of the difference in action of the spherical and parabolic reflectors.

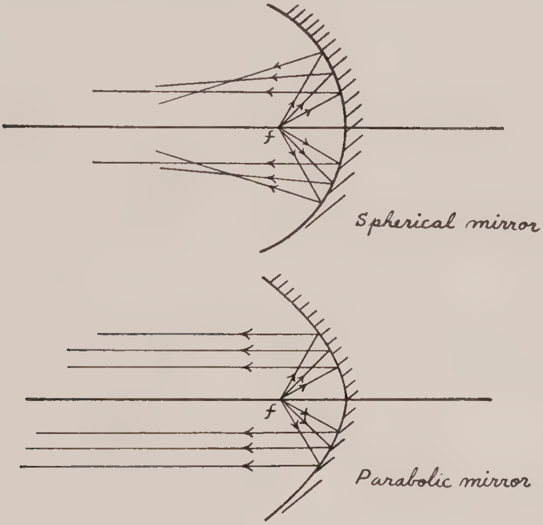

FIG. 53. Spherical and Parabolic Mirror.

The Refraction of Light from a Spherical Surface.—In Fig. 54 a spherical refracting surface is shown, the center being at C and vertex at V. A point object O lies in a medium of refractive index n_1.

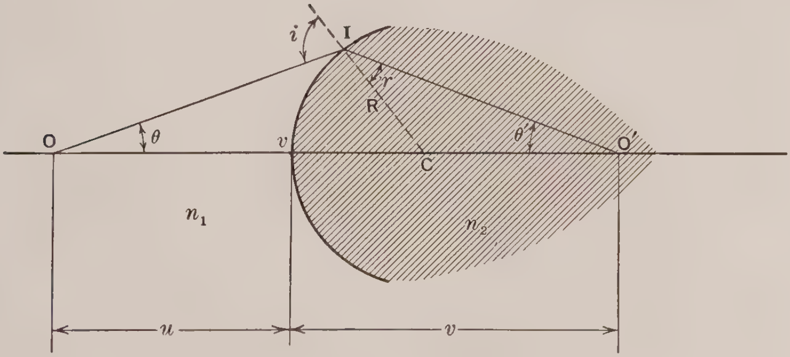

FIG. 54. Refraction at Spherical Surface.

Its image O' is formed in the second medium having an index of refraction n_2, the boundary surface between the two media being spherical. Let OO' represent the axis of this system and the point V the vertex of the refracting surface. Θ and Θ' are the so-called slope angles of the rays OI and IO'. The law governing the formation of image O' from object O in this case may be stated as

$$\frac{n_1}{u} + \frac{n_2}{v} = \frac{n_2 - n_1}{R}$$

where u is the object distance, v the image distance, n_1 and n_2 the indices of refraction of the first and second media respectively, and R the radius of the spherical boundary surface between these two media.

The Thin Lens in Air.—Fig. 55 represents a thin lens bounded by two spherical surfaces having vertices at V_1 and V_2. The image of an axial point object O is represented by O'. Let OV_1 and V_2O' equal u and v, respectively. Since it is assumed that this lens is to be used in air, n_1 and n_3 will equal unity. For the sake of convenience, let $n_2 = n$, the index of refraction of the lens material. Under these conditions, the law governing the formation of image O' may be stated

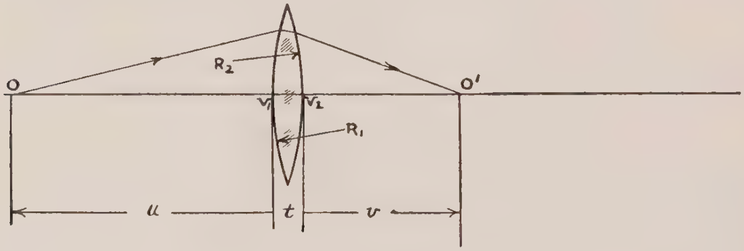

FIG. 55. Imagery by Thin Lens.

$$\frac{1}{u} + \frac{1}{v} = (n - 1)\left[\frac{1}{R_1} - \frac{1}{R_2}\right].$$

The derivation of this equation, as given in any reliable text on geometrical optics, is made on the assumption that t, the thickness of the lens, is zero. Since this is an obvious impossibility, this equation must be regarded as an approximation to be used only in those cases where the actual thickness of the lens is a small percentage of its focal length. A later section (see page 64) offers a more extensive analysis for use in those cases where the lens thickness itself is of sufficient size to be important.

Figure 56 shows the various types of spherical thin lenses encountered in practice. Those shown on the top row of this figure are so-called converging lenses, since a pencil of light falling upon one of these is made more convergent. A converging lens, frequently called a positive lens, is characterized by the fact that it is thicker at the center than at the edges and therefore has a positive focal length. Diverging or negative lenses, on the other hand, are always thinner at the center than at the edge. A pencil of light incident upon a diverging lens is rendered more diverging, thereby producing a virtual image. Fig. 57 shows the action of both a converging and a diverging lens upon a parallel beam of light. It will be noted that the converging lens forms a real image at a distance *f* from the lens and on the opposite side from the source. The diverging lens, on the other hand, forms a virtual image at a distance *f* from the lens but on the same side as the source.

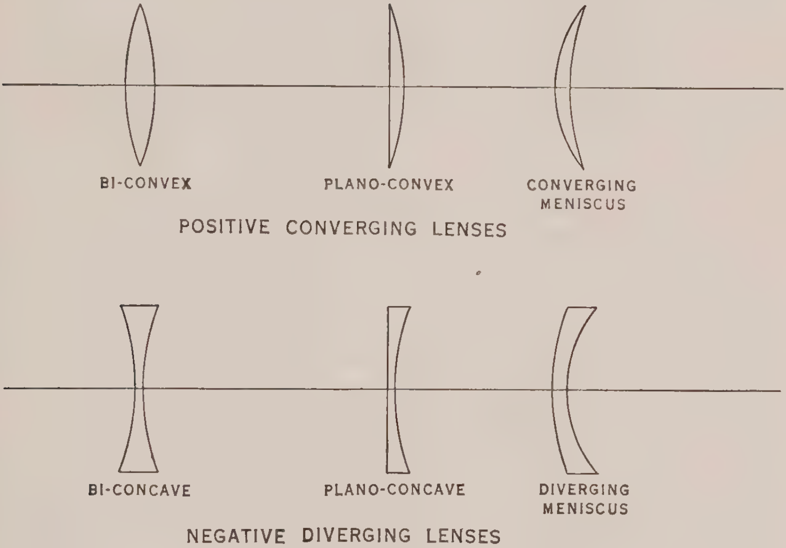

FIG. 56. Types of Spherical Lenses.

Magnification Produced by a Thin Lens.—So far, only the images of points lying on the optical axis of the lens have been considered. Fig. 58 shows an object *h* (represented by an arrow), located at a distance *u* from the lens. The image of this object may be located by tracing two rays from the top of the arrow, the one ray *OA* being parallel to the optical axis, while the other, *OC*, is directed toward the optical center of the lens. At point *A*, the ray *OA* will be refracted through the focal point *f* and will therefore continue in the image space in the direction *If*. The ray *OC*, however, will pro-

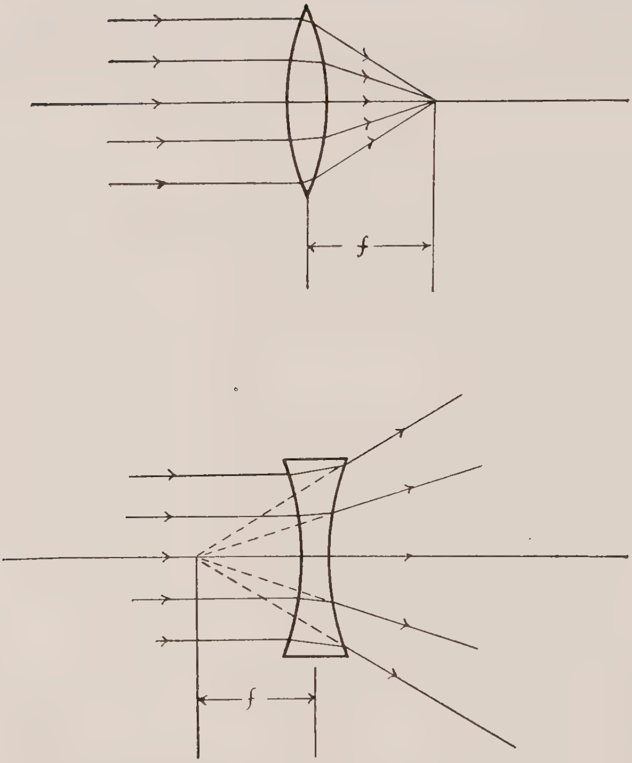

FIG. 57.

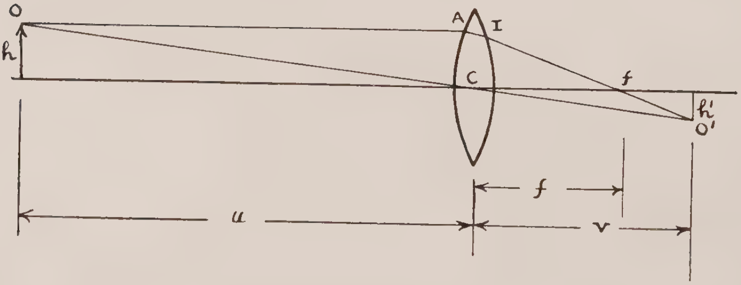

FIG. 58. Magnification of a Thin Positive Lens.

ceed unrefracted in the direction CO', where OCO' is a straight line. Since the rays IO' and CO' intersect at point O' this may be regarded as the image of point O. The image h' is an inversion of the object h, and, in general, it will differ in size from the object.

If h and h' represent the height of object and image respectively, the magnification produced by the thin lens may be said to equal h'/h. It will be observed from the geometry of Fig. 58 that the magnification produced by the thin lens is also equal to v/u. Fig. 59 indicates the relation between object and image for a positive converging lens when the object is located within the focal length of the lens. Here the image is much enlarged, erect, and on the same side of the lens as the object, that is, a *virtual* image. Such is the action produced by a simple magnifying lens or reading glass.

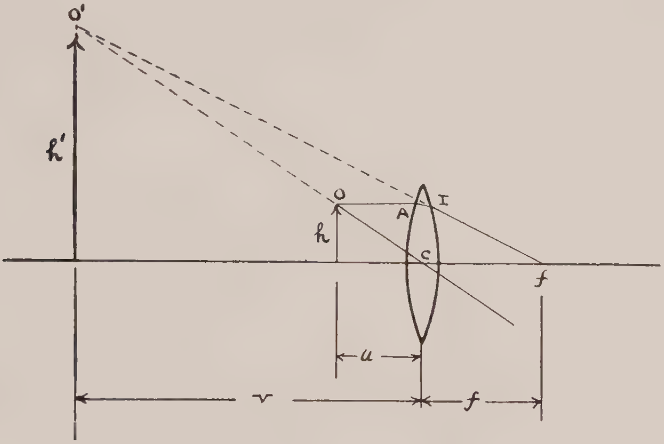

FIG. 59. Magnification of Thin Positive Lens.

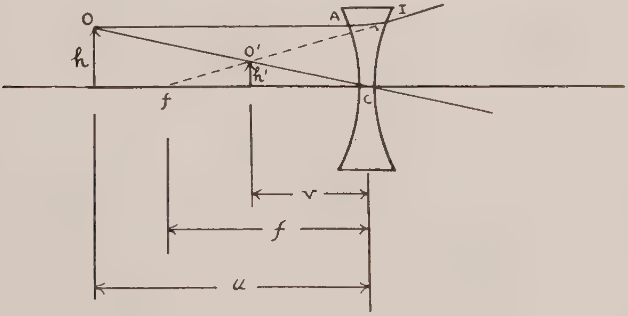

FIG. 60. Thick Lens in Air.

Figure 60 shows the image formed by a diverging lens. In the case shown, the image is virtual, erect, and smaller than the object. Therefore, a diverging lens makes objects look smaller. It has the compensating advantage, however, that the field of view has been considerably enlarged.

The Diopter.—The dioptric power of a lens is equal to the reciprocal of its focal length in meters, that is, $D = 1/f$. Therefore, a lens whose focal length is one meter has a strength of one diopter. Likewise, a lens whose focal length is one-half meter has a power of two diopters, etc.

Systems of Thin Lenses.—The final image produced by a system of thin coaxial lenses is found by using the image produced by the first lens as the object of the second lens, etc. throughout the system. A somewhat simpler and more direct method is to compute the focal length of the combination of thin lenses and treat the combination as a single lens. This may be obtained by dividing the continued product of the focal length of each of the lenses in the system by the sum of their focal lengths provided the lenses are in intimate axial contact. When large gaps exist between the individual lens elements, the former method outlined above must of necessity be used.

The Thick Lens in Air.—For those cases where the thickness of the lens is a substantial portion of the focal length, the approximate formulae given in the preceding sections are inadequate. When this is the case, the formula

$$\frac{1}{u} + \frac{1}{v} = \frac{1}{f}$$

may be used, provided u and v are measured from the two *principal points* of the thick lens, and if for f we use the "*equivalent focal length.*" Points P_1 and P_2 in Fig. 61 are the two principal points for the biconvex lens shown. The equivalent focal length in this case is

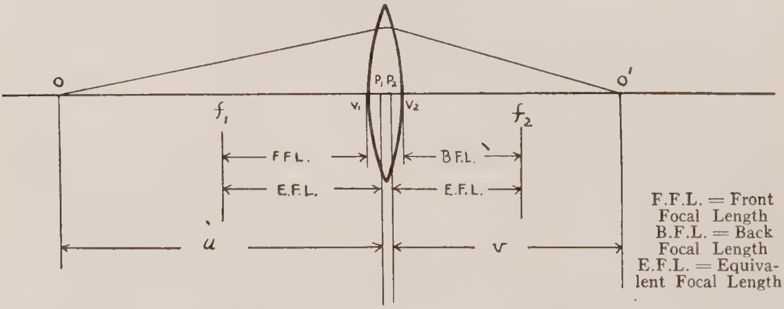
O
P₁ P₂
O'
f₁
V₁
V₂
f₂
F.F.L.
B.F.L.
E.F.L.
E.F.L.
u
v
F.F.L. = Front Focal Length
B.F.L. = Back Focal Length
E.F.L. = Equivalent Focal Length

FIG. 61. Thick Lens in Air.

the distance E.F.L. It will be noted from examining Fig. 61 that u and v are measured from the two principal points.

The principal points of any lens lie on the axis and are conjugate one to another, that is, one point is the image of the other. Hence, an entrance beam which passes through the first principal point converges from the second principal point and is parallel to the entrance beam. The location of the two principal points and the equivalent focal length of a thick lens may be computed according to the equations given below:

$$V_1P_1 = \frac{tR_1}{n(R_1 - R_2) - t(n-1)},$$

$$V_2P_2 = \frac{tR_2}{n(R_1 - R_2) - t(n-1)},$$

$$\text{E.F.L.} = \frac{nR_1R_2}{(n-1)[n(R_2 - R_1) + t(n-1)]}.$$

The quantity t represents the thickness of the lens, n the index of refraction of the glass, and R_1 and R_2 the radii of the front and rear lens surfaces.

A biconvex or biconcave lens with surfaces of equal curvature have the two principal points located at equal distance from the two vertices. When one surface is more strongly curved than the other, both principal points tend to move toward the more strongly curved surface. When one surface of the lens is plane, one principal point lies at the vertex of the curved surface. The principal points for a meniscus lens usually lie entirely outside of the lens.

From Fig. 61 it will be observed that a thick lens has three focal lengths: the *back focal length,* the *front focal length,* and the *equivalent focal length.* The equivalent focal length represents the focal length of a thin lens which would have the same strength as that of the thick lens being computed. It will be observed that the back focal length and the front focal length are measured from the lens surfaces instead of from the principal point.

Planes erected through the principal points of a lens orthogonally to the lens axis are known as principal planes, or planes of unit magnification. Fig. 62 indicates a method of locating an image formed by a thick lens. Here the planes P_1 and P_2 are the principal planes of the lens. With O as the object, the ray OP_1 will emerge at P_2, the ray P_2O' being parallel to OP_1. Likewise, the ray OA, which is parallel to the axis, will emerge at A', passing through the focus f and continuing to the image point O'. The intersection of ray P_2O' and $A'O'$

locates the position of image O'. Here again, the ratio between h' and h is the magnification produced by the lens.

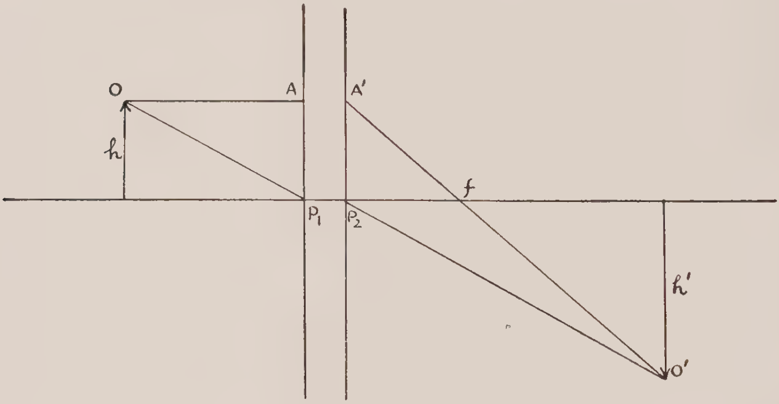

FIG. 62. Method of Locating Image.

Combination of Thick Lenses.—When two thin lenses of focal length f_1 and f_2 are placed in contact, the focal length of the combination is given by

$$F = \frac{f_1 f_2}{f_1 + f_2}.$$

When thick lenses are used, however (or thin lenses which are not in contact), the effective focal length of the lens system is given by the following equations:

$$F = \frac{f_1 f_2}{f_1 + f_2 - a}.$$

Here f_1 and f_2 are the equivalent focal lengths of the two thick lenses and a is the distance from the second principal point of the first lens to the first principal point of the second lens.

The action of two thin lenses may be considered equivalent to a single thick lens having equivalent focal lengths as given by the foregoing equation and two principal points as located by the two following equations:

$$p_1 P_1 = \frac{a f_1}{f_1 + f_2 - a},$$

$$p_2 P_2 = \frac{a f_2}{f_1 + f_2 - a}.$$

In the foregoing equations, p_1P_1 represents the distance from the first principal point of the first single thick lens to the principal point of the equivalent thick lens; and the distance p_2P_2 that from the second principal point of the second component lens to the second principal point of the equivalent lens.

Entrance and Exit Pupils.—Let us consider the action of two thin lenses between which is placed a diaphragm or stop. Such a system is shown in Fig. 63. This is representative, in an elementary sort of way, of the construction of a typical photographic objective.

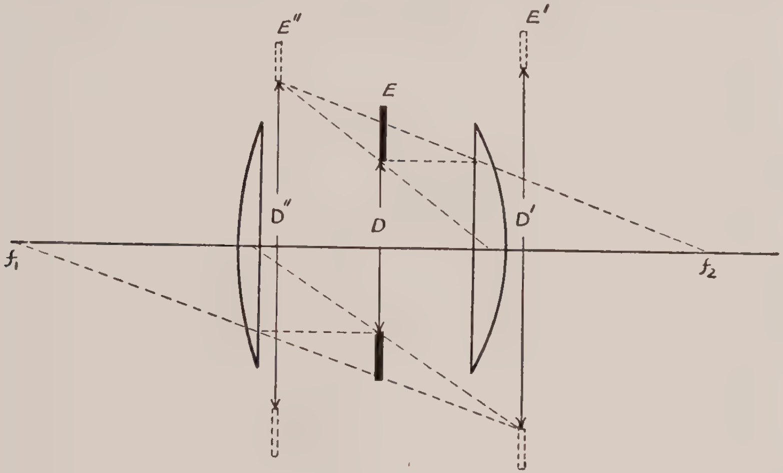

Fig. 63. Imagery of Entrance Pupil.

D = actual diameter of diaphragm.
D' = diameter of the "entrance pupil."
D'' = diameter of the "exit pupil."

When an objective of this type is examined from the object side, the size of the diaphragm appears to be that of E' rather than E, where E' is the image of E as formed by the front lens. Likewise, when E is examined visually from the rear of the objective, it appears to be of size E'' instead of E, where in this case E'' is the image of E as formed by the second lens. According to the nomenclature developed by Abbe, E itself is known as the aperture stop while E' is called the *entrance pupil* and E'' the *exit pupil.*

Although the entrance and exit pupils in Fig. 63 are larger than the actual aperture stop, such need not necessarily be the case. In any well-designed photographic objective, however, the aperture stop is usually smaller than either the entrance or exit pupil, that is, it is smaller than the images of this aperture stop as formed by the front and rear lens elements respectively. It should be noted that the entrance and exit pupils E' and E'' may be found directly by using E as an object and determining its image as formed by the first and second lenses respectively.

Relative Aperture.—The speed or light-gathering power of a photographic objective is usually spoken of in terms of the so-called *relative aperture*. Relative aperture is arbitrarily defined as the ratio between the focal length of the lens and the diameter of its entrance pupil.

$$\text{R.A.} = \frac{f}{D'}$$

where R.A. = relative aperture or f/number,
f = focal length,
D' = diameter of the entrance pupil.

Therefore, if a lens has a focal length of 100 millimeters and the diameter of the entrance pupil is 20 millimeters, its relative aperture, or speed, is equal to $100/20 = 5$. That is, the lens has a rated speed of $f/5$.

Most high-grade photographic objectives are equipped with adjustable aperture stops, commonly known as iris diaphragms. When this is the case, the speed, or light-gathering power, of the objective may be changed at will simply by changing the diameter of the iris diaphragm. In this way the denominator of the f/number equation given above becomes variable; therefore the speed of the lens is adjustable at the will of the user. For example, if the diaphragm is stopped down to 10 mm. instead of 20 the speed of the objective changes from a value of $f/5$ to a new value of $100/10 = f/10$. Since the lens has been stopped down, thus decreasing the diameter of the aperture, it would necessarily be slower, that is, gather less light. Consequently, a speed of $f/10$ is slower than a speed of $f/5$, the difference in speed being proportional to the change in area of the entrance pupil. Since the areas of circles are directly proportional to the squares of their diameters, it follows that the speeds of photographic objectives are inversely proportional to the squares of their $f/$ numbers. Hence a lens operating at $f/5$ is four times faster than the same lens operating at $f/10$.

Although the f/number system is now universally used throughout the world, years ago some lenses were marked on the U. S. (Uniform

System). In the U. S. system, the numbers are directly proportional to the exposure required, *f*/4 being taken as unity. A comparison between the *f*/number system and the U. S. system is given below:

f/number	*f*/4	*f*/4.5	*f*/5.6	*f*/6.3	*f*/8	*f*/11	*f*/16	*f*/22	*f*/32	*f*/45
U. S.	1	1.26	2	2½	4	8	16	32	64	128
Relative exposure required	1		2		4	8	16	32	64	128

Experimental Determination of Relative Aperture.—When the focal length of a photographic objective is known, it is only necessary to determine the diameter of the entrance pupil in order to find its relative aperture. The diameter of the entrance pupil may easily be found experimentally by a process devised by A. Steinheil. After the camera is set on the infinity mark, the ground glass is removed and replaced by an exactly-fitting piece of cardboard which has a small circular hole about two millimeters in diameter at its center. Care should be exercised in fitting the piece of cardboard, since the hole at its center should coincide with the optical axis of the lens. In the darkroom a small piece of bromide paper is fitted inside the lens cap, and this is placed over the front of the lens with the emulsion side of the paper toward the lens. An incandescent lamp is now held behind the hole in the cardboard for a few seconds. A black circular disk will be found upon the bromide paper upon development, the diameter of this circle being equal to the entrance pupil of the objective. This will be seen readily by studying the course of rays from the small circular aperture in the cardboard. The *f*/number, or speed of the lens, is now readily found by dividing its focal length by the diameter of the black circle appearing on the bromide paper.

Angle of View.—The angle of view of any objective is the angle subtended by two lines drawn from the node of emergence to the corners of the plate in use. The shorter the focal length of the lens in relation to the size of the plate, the greater the angle of view and the more of the subject included from a given viewpoint.

It is often of advantage to be able to calculate the maximum angle of view for a given lens on a certain sized plate, and to render this a simple matter we have reproduced a chart by which this information can be simply and rapidly secured.

The maximum angle of view possible with any lens depends upon the relation between its focal length and the size of the plate which it will cover with satisfactory definition. For a given size of plate, the shorter the focal length of the lens, the greater is the angle of view, while on the other hand, the larger the plate which a lens of given focal length will cover with sufficiently critical definition, the greater is its angle of view. Thus a lens of six inch focal length will include a much greater angle if used on a 5 × 7 plate than if used on a 4 × 5 plate. Most lenses, however, particularly if of high speed, will not cover satisfactorily a plate much larger than that for which they are designed unless considerably stopped down. A lens made to cover with satisfactory definition a field large in proportion to its focal length is termed a wide angle lens.

Depth of Field.—Theoretically, even a high-grade photographic objective is incapable of forming a sharp image of more than one plane in the object space. In practice, however, not only the subject focused upon appears sharp, but subjects somewhat nearer and those much farther away also appear tolerably sharp. The distance from the nearest to the farthest points that appear sharp is called the *depth of field* of the objective. The depth of field of a given lens depends upon (1) its focal length; (2) its relative aperture; (3) the distance of the lens from the plane focused upon; (4) the diameter of the permissible circle of confusion; and (5) the presence of various lens aberrations.

In general, the image created by even a theoretically perfect lens does not fall upon a flat plane unless the object photographed is a flat plane. Therefore, we must consider the image formed when photographing a three-dimensional object as also being three-dimensional. For example, in Fig. 64 let us consider that *A* and *B* represent two

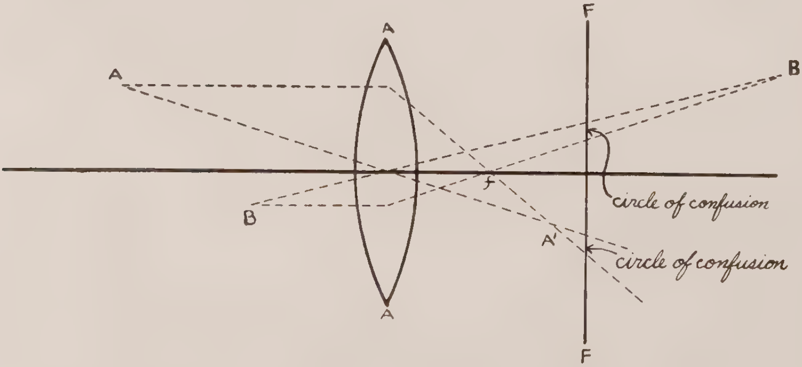

Fig. 64.

points in the object being photographed. A lens AA forms images at these points as A' and B', respectively. It is obvious that no flat plane perpendicular to the optical axis can be drawn which will include both points A' and B'. Therefore, it is impossible to place a film in the image space which can record both of these points at the same time and still have the film orthogonal to the optical axis. If the film were located in some such plane as FF, then the images of points A and B in the film plane would be recorded as disks rather than points. A disk of this sort is called a circle of confusion.

If the circle of confusion is small enough, it is indistinguishable from a point. Therefore, the actual point image may fall slightly in front of, or slightly behind, the image plane without producing a blur. Fig. 65 shows the imagery of two axial point objects A and B at A' and B' respectively. If the maximum permissible circle of confusion is represented by d, then the planes X' and Y' represent the limits within which the film may be placed without exceeding a circle of confusion greater than d. This permissible film range is known as the *depth of focus,* while the conjugate range in the object space is termed the *depth of field.* Hence in Fig. 65 the distance XY is the depth of field and the

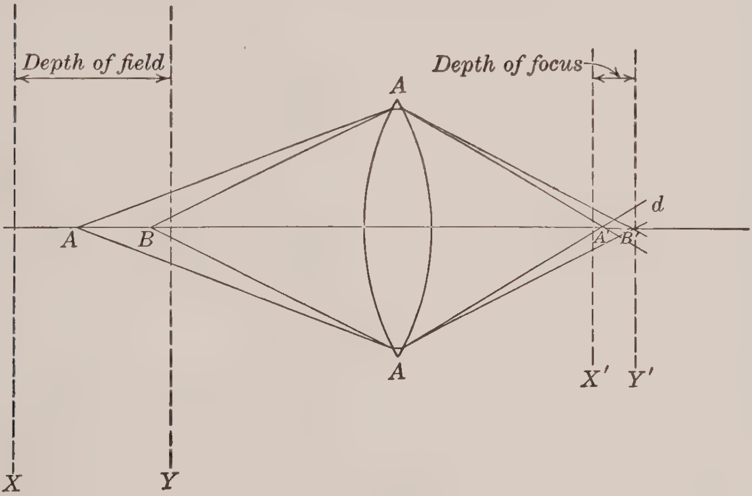

Fig. 65. Depth of Field and Depth of Focus.

Brown—Theory and Practice of Depth of Focus. Brit. J. Phot. **69** (1922) 492, 507, 521, 534.

Southworth—Numerical Expression for the Depth of Focus. Brit. J. Phot. **76** (1929) 483–486.

distance $X'Y'$ the depth of focus, provided the circles of confusion on the film do not exceed an amount which may be tolerated by the eye.

Depth of Field and Hyperfocal Distance.—The manufacturers of photographic objectives usually allow a circle of confusion whose diameter equals 1/1000 of the focal length of the lens in computing depth of field tables. Hence, for a 2-inch lens the tolerable circle of confusion would equal 1/500 of an inch, while for a 10-inch lens the circle of confusion would be 1/100 of an inch. This method of selecting the permissible circle of confusion compensates automatically for the fact that the shorter focal length lenses are used on miniature cameras where enlargements are almost inevitably made from these negatives.

In computing depth of field tables it is customary to utilize the so-called *hyperfocal distance.* When a camera is focused on the hyperfocal distance, all objects within the range from infinity to a position half way between the camera and the hyperfocal point appear to be in focus. A lens is said to exhibit its maximum depth of field for a given aperture when it is focused upon the hyperfocal distance. A knowledge of the hyperfocal distance for a given lens at its various apertures prevents unnecessary stopping down in order to secure maximum depth of field. The hyperfocal distance of a given objective may be computed by means of the following equation:

$$H = \frac{F^2}{(f/\text{number})\, d}$$

where H represents the hyperfocal distance in inches, F the focal length of the lens in inches, and d the diameter of the circle of confusion in inches ($d = F$ divided by 1000).

After having computed the hyperfocal distance, the near and far distant points of sharpness may be computed in accordance with the following formulas:

$$\text{nearest point of sharpness} = \frac{Hx}{H + x},$$

$$\text{farthest point of sharpness} = \frac{Hx}{H - x}.$$

Where x = distance focused on.

To illustrate the use of these formulas, consider the case in which a photograph is made using a lens having a relative aperture of $f/8$ and a focal length of 10 inches, the object being 20 feet from the camera and a circle of confusion of 1/100 of an inch being regarded as permissible. In this case,

$$H = \frac{F^2}{(f/\text{number})\,d} = \frac{10^2}{8 \times 1/100} = 1250'';$$

$$\begin{aligned}\text{nearest point of sharpness} &= \frac{Hx}{H + x}\\ &= \frac{1250 \times (20 \times 12)}{1250 + (20 \times 12)}\\ &= 201.8''\\ &= 16' - 9''.\end{aligned}$$

$$\begin{aligned}\text{farthest point of sharpness} &= \frac{Hx}{H - x}\\ &= \frac{1250 \times (20 \times 12)}{1250 - (20 \times 12)}\\ &= 297''\\ &= 24' - 9''.\end{aligned}$$

Hence, as measured from the camera, the depth of field extends from 16 feet 9 inches to 24 feet 9 inches and, therefore, the zone of sharpness extends 3 feet 3 inches in front of the object and 4 feet 9 inches beyond it. It will be noted that the depth of field is not equal on both sides of the object.

The point on which to focus in order to obtain sharp definition on two objects at different distances from the camera without unnecessary stopping down can be determined by a very simple calculation which usually can be done mentally. The rule is to multiply the two distances, double this, and divide by the two added together. Thus, if the two objects are placed 4 and 6 feet from the camera, the point on which to focus would be found as follows:

$$\frac{4 \times 6 \times 2}{4 + 6} = \frac{48}{10} = 4.8 \text{ ft.}$$

Focus on this distance using the lens at its largest aperture and then reduce the aperture until the two objects are sharp. By knowing the exact point on which to focus, the use of a stop smaller than absolutely necessary is avoided.

A simple chart, due to Wright, from which, by the application of a straight edge, not only the distance on which to focus, but also the lens aperture, given the distances within which sharp focus must be obtained is shown in Fig. 66.[5] A straight edge applied across the scales

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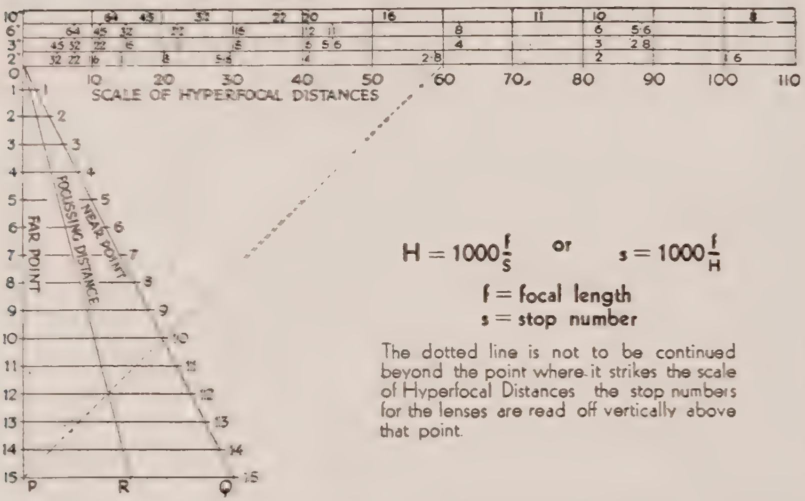
[5] *Brit. J. Phot.* **83** (1936) 609.

OP and *OQ* intersects on *OR*, the distance on which to focus and on the scales at the top the lens aperture required with lenses of 2, 3, 6 and 10 inches focal length. The scale may be used for any multiple of the distances indicated by multiplying all distances by the common multiple and by dividing the indicated lens multiple. Thus, if the distances on the scale must be multiplied by ten, the lens aperture is divided by ten so that *f*/11 becomes *f*/1.1.



$$H = 1000\frac{f}{s} \quad \text{or} \quad s = 1000\frac{f}{H}$$

f = focal length
s = stop number

The dotted line is not to be continued beyond the point where it strikes the scale of Hyperfocal Distances the stop numbers for the lenses are read off vertically above that point.

Fig. 66. Chart for the Determination of the Distance on which to Focus (Wright).

Lens Aberrations.—The mathematical relations used to locate the image formed by a lens are based on the assumption that the marginal rays come to the same focal point as the axial rays. When an

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Collins—Depth of Focus and its Graphical Representation. Brit. J. Phot. **67** (1920) 659, 676.

Lee—Chart for Finding the Depth of Focus. Phot. J. **62** (1922) 229; Brit. J. Phot. **69** (1922) 135.

Brown—A Simple Depth Chart. Brit. J. Phot. **70** (1923) 775.

Jones—Depth of Field Determination. Phot. Tech. **1** (1939) Oct. p. 17.

Jacroux—Photo-Revue. **49** (1937) 289.

Liesegang—Depth of Field Calculations. Phot.Tech. **1** (1939) Oct. p. 48.

Eriksen—Depth of Field. American Annual of Photography **54** (1940).

Gordon—Depth of Focus in a Nutshell. Amer. Phot. **31** (1937) 112, 114.

Gage—Focusing Scales and a Graphical Method of Handling Depth of Focus. Amer. Annual of Photography **52** (1938) 181.

Wheeler—Chart for Lens Calculations. Phot.Tech. **2** (1940) Feb. 31.

actual lens is examined in practice, however, it is found that this is not the case. The failure of all the rays to converge to a common point after refraction results in a lack of perfection in imagery which is referred to as lens aberration. In other words, the presence of aberrations causes object points to be imaged not as points but as small finite areas of light, the size of these areas being directly proportional to the magnitude of the aberrations present. It is obvious that the smaller these areas become (through skillful lens design) the sharper the resulting image. It, therefore, becomes the problem of the lens designer to reduce these aberrations to a minimum in order that the image may be as sharp as possible.

The presence of aberrations in a lens arises from several different causes, each of which may be spoken of separately although in practice the aberrations seldom exist alone. The aberrations which are commonly considered separately are: spherical aberration, chromatic aberration, coma, astigmatism, distortion, and curvature of field.

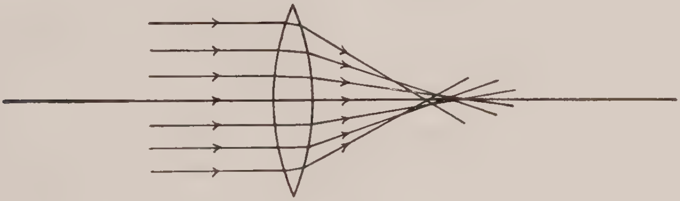

FIG. 67. Spherical Aberration.

Spherical Aberration.—Fig. 67 represents the type of image obtained with a lens having considerable spherical aberration. It will be noticed that the marginal, or rim, rays come to focus nearer the lens than the axial rays,—in other words, the rays passing through the lens do not cut the axis at a single point. In a single positive lens the rays farthest from the axis come to focus closer to the lens, while in a negative lens the opposite is true. Hence, the combination of a positive and negative lens of proper strength may be used to eliminate spherical aberration. Another but somewhat more expensive method of correctting spherical aberration is to form a non-spherical surface the shape of which will cause all the rays to come to a single point of focus. A single lens of this type is known as an aspheric lens. From this it is

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SALT—Graphic and Simple Method of Demonstrating Some Aberrations of Lenses. Brit. J. Phot. **76** (1929) 308.

evident that spherical aberration is due to the surface of the lens being spherical.[6]

The combination of a positive and negative lens to neutralize spherical aberration is a common procedure used by lens designers to overcome this inherent difficulty encountered with spherical glass surfaces. In the manufacture of photographic objectives, it is common practice to adhere to plane and spherical surfaces and to minimize spherical aberration by the proper choice of radii of curvature for the lens surfaces. A plano-convex lens used with its convex surface toward the incident light gives far less spherical aberration than almost any other type of single lens, particularly where parallel light is incident upon the convex surface.

It is usually considered satisfactory if a photographic objective exhibits no more spherical aberration than an amount equal to approximately one-third of one per cent of its focal length. Therefore, in a 100-mm. lens marginal rays focusing at 3/10 of a mm. in front of the axial rays would be tolerated.

Chromatic Aberrations.—We have previously shown that the focal length of a single lens may be represented by the equation:

$$f = \frac{1}{(n - 1)\left(\frac{1}{R_1} - \frac{1}{R_2}\right)} .$$

As pointed out on page 54 the index of refraction n of any optical glass is different for light of different wave lengths. From this it follows that any single glass lens has a different focal length for each color of the spectrum. This effect is known as chromatic aberration. With a simple positive lens the focal length is shorter for blue light than for red, because all glasses exhibit a higher value of n for blue light than for red light. With a negative lens, however, the opposite is true and the focal length is shorter for red than for blue. Therefore, chromatic aberration may be corrected by making a compound lens of two separate lenses, one positive and the other negative, provided they are of the proper strength and correct indices of refraction. In practice, the positive lens is usually made of crown glass and the negative lens of flint. With flint the index of refraction varies by a considerable amount from color to color, while the effect is not so marked with crown glass. In design the negative flint lens is so made that its variation of focal length with color is sufficient to compensate for the focal length color variation in the crown lens. By using flint glass for the negative lens, the converging effect of the positive component is not entirely neutralized and the resulting combination is a positive lens in which chromatic aberrations have been eliminated. In practice, the adjacent surfaces of the two components are given the same curvature which enables them to be cemented together with Canada balsam. This cement makes the two lenses a single unit eliminating the reflection losses which would be present at the inner surfaces were they separated.

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[6] Aspherical surfaces are used to a limited extent in the manufacture of condenser lenses where the improvement in imagery justifies the large expense entailed by the handwork that must be done in shaping such a lens surface. This technique is usually resorted to only in those cases where the maximum amount of light must be passed by the condensing lens and one cannot afford to lose the rim ray component.

Formerly, when photographic plates were only blue sensitive, the problem of chromatic aberration did not assume the importance that it does today with supersensitive panchromatic emulsions sensitive to light of all colors. Also, for color photography it is particularly important that the photographic objective be free from chromatic aberration to eliminate color fringing. Today the problem of correcting for chromatic aberration transcends in importance all other corrections if the lens is to be used for color photography.

A doublet lens consisting of a positive and negative element which have been achromatized to eliminate chromatic aberration is known as an achromat.

Astigmatism.—Fig. 68 indicates the manner in which an oblique parallel beam of light incident upon a single positive lens is brought to focus. When an oblique light beam of this nature is passed through a positive lens, a loss of perfection in imagery results known as astigmatism. The type of image formation can be understood best by considering the appearance of the image formed on a ground glass which is held in the neighborhood of the point of focus. If the ground glass is held at point *A*, the image is an erect vertical line; at an intermediate point the image is an ellipse. At a point midway between *A* and *B* the image is a circle, while at *B* the image again is a straight line but this time a horizontal one at right angles to the line image formed at point *A*. The thumb-nail sketch illustrates the type of images formed in the neighborhood of focus where astigmatism is present.

HERRIOTT—A Method of Measuring Axial Chromatic Aberration in an Objective Lens. J. Soc. Mot. Pict. Eng. **20** (1933) 323–331.

The effect of astigmatism upon the image of an object containing horizontal and vertical lines is interesting. If the negative plane is so located that horizontal lines are in focus, then vertical lines are out of focus and vice versa. In other words, either vertical or horizontal lines can be focused sharply, but both cannot be in focus simultaneously.

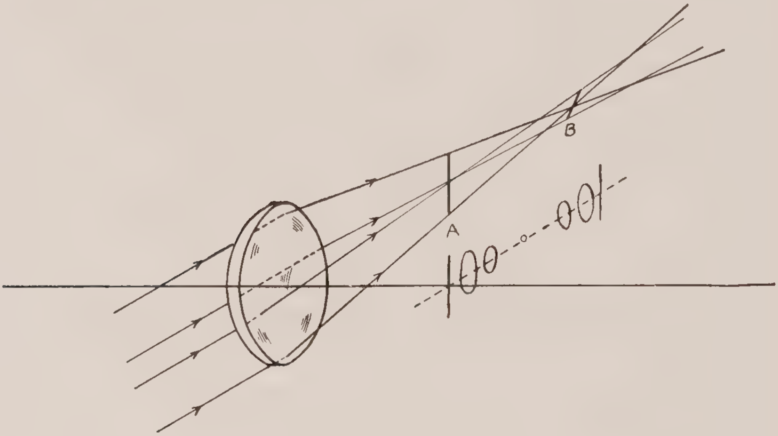

Fig. 68. Astigmatism.

In practice, astigmatism is lessened by the use of compound lenses having glasses of properly selected indices and by using a combination of spherical surfaces which bear the proper relation to each other. It should be borne in mind that astigmatism is an off-axis characteristic, and when an image is being examined for astigmatic defects the marginal regions rather than the center should be scrutinized. A wire mesh screen photographed against a blue sky offers a very convenient subject to photograph when testing a lens for astigmatic defects. If astigmatism is present, the horizontal wires are sharp at one point of focus while the vertical lines are definitely out of focus. The reverse is true for a slightly different image plane.

Coma.—When a bundle of rays pass obliquely through a single lens, it frequently happens that the rays in the neighborhood of the image come to a focus in approximately the same plane but fall at different points instead of being superimposed. When this occurs, the lens is said to suffer from coma.

Figure 69 shows a comatic image. For the sake of clearness let us consider the lens to be divided into several circular concentric zones.

The image formed by the zone nearest the axis is represented by the small circle at A. The image formed by each successive zone is a slightly larger circle of confusion and displaced to the right. It is evident that most of the light is concentrated in the region of the smallest circle, and as a result the image is brightest at its small end and falls off in intensity toward the larger end. The resemblance of this image to that of a comet is responsible for the name of this aberration.

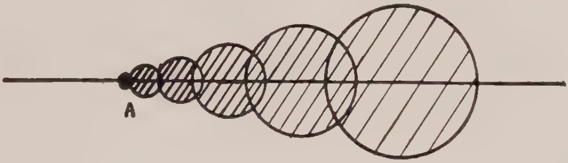

Fig. 69. Coma.

Coma is sometimes referred to as the spherical aberration of oblique rays. Like astigmatism it occurs at the margins of the image field rather than at its center. In considering both astigmatism and coma it should be remembered that only the simplest possible case has been presented here, and we have assumed that all other aberrations are absent. For a further discussion of this subject the reader is referred to any of the many reliable texts on optics. The elimination of coma from a compound lens is accomplished by cementing together single negative and positive lenses each of which suffers from coma but in the opposite sense. In practice, it is almost impossible to correct for coma in all the circular zones of the lens. Therefore, a lens is said to be coma free when it exhibits no coma for some particular zone and the amount of coma in other zones is reduced to a negligible amount. A doublet lens which is free from both spherical aberration and coma for some particular point is referred to as an *aplanat.*

Curvature of Field.—Curvature of field and distortion differ fundamentally from the four aberrations already discussed in that they do not pertain to the perfection of the imagery of an object point. Curvature of field and distortion refer to the relative location of different image points as compared with the relative location of the object points. In other words, curvature and distortion refer to the spacial arrangement of the image points rather than to their degree of perfection. When the image points of a plane object lie upon a curved surface rather than a plane, the lens is said to suffer from curvature of field. Fig. 70 represents such a condition. This type of aberration is particularly disadvantageous in photographic objectives since photographic materials are, in general, confined to plane surfaces, thereby making it impossible to focus the entire object sharply upon the sensitive material. Curvature of field may be corrected to some extent by using a combination of two lens elements of proper indices. Much more can be done, however, to minimize this aberration by separating the elements and placing a diaphragm of the proper size between them. An excellent example of this may be seen by examining the field of a single lens and comparing it with the field produced by a combination of two lenses, one positive and the other negative, the combination, however, having the same focal length as the single lens. A stop, or diaphragm, located at a suitable distance in front of a simple meniscus lens tends to flatten the field quite effectively. This procedure is known as artificially flattening the field, a technique employed in the manufacture of many inexpensive lenses. This effect is produced by the action of the diaphragm in causing the rays forming the image at the edge and the center of the field to traverse different portions of the lens.

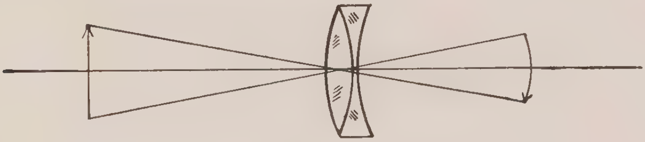

Fig. 70.

Distortion.—When a square object is imaged in the manner shown at *A* or *B* in Fig. 71 the lens producing this image is said to suffer from distortion. Distortion arises from the fact that the linear magnification varies with the distance from the axis. If the magnification is greater at the margin of the field of view than at its center, as shown at *A*, positive distortion results; while if the magnification is greater at the center of the field than at its edges, negative distortion results, as shown at *B*. The terms *pin cushion* and *barrel* distortion are usually associated with the type of images formed at *A* and *B* respectively.

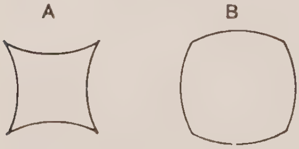

Fig. 71. Types of Distortion.

The type of distortion as well as its magnitude depends largely upon the position of the diaphragm. Fig. 72 illustrates the effect of diaphragm location in the case of a plano-convex lens. It will be noted that when the diaphragm is placed in front of the lens, barrel distortion results, while if the diaphragm is located behind the lens, pin cushion distortion is shown. The third diagram shows an effort to combine these two opposite errors. When the diaphragm is placed at the proper point between the two lenses, the positive error of the first lens will be neutralized by the negative error of the second and a rectilinear, or non-distorted, image is produced. In a well designed photographic objective, the amount of distortion seldom exceeds 3/10 %, even for angular distances as great as 30 degrees from the axis. Symmetrical objectives of the rapid rectilinear type exhibit little or no distortion since they are constructed symmetrically about the diaphragm.

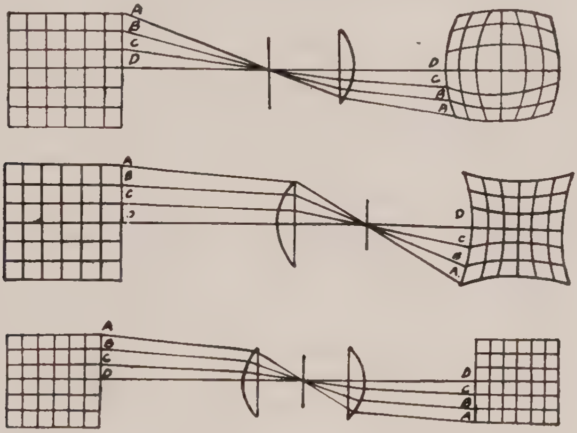

FIG. 72. Effect of Stop or Distortion.

Balancing Aberrations in Lens Design.—In any specific photographic objective it is impossible to eliminate certain imperfections which of necessity must be present,—in fact no optical system has as yet been devised which eliminates even a single aberration completely for even a single position of the object. The best that the lens designer can do is to balance the aberrations to produce a lens which is useful for the purpose intended and at the same time not requiring too many elements thereby making it difficult to manufacture. Usually the lens designer develops a lens to eliminate, insofar as possible, those aberrations which would be most detrimental. With this in mind, he so selects the components, and so shapes them, that these aberrations will be reduced to a minimum and at the same time none of the others will reach such a magnitude as to become objectionable. Usually, if the demands of the user are such that the relative aperture and size of field to be covered are not excessive, the aberrations can be so controlled that the quality of the image is limited solely by the finite nature of a wave length of light. Even in the case of wide-angle, high-aperture lenses, the designer usually produces an objective which is superior in its image formation qualities to the skill of the user.

Resolving Power.—As previously pointed out, a study of the nature of light reveals it to be of a wave character. It is a commonly observed phenomenon that waves, for example, ocean or water waves, bend around the end of a breakwater thereby invading that portion of the water surface which would normally be completely sheltered if the waves travelled only in straight lines. An opaque body, such as a diaphragm or stop, may be considered as an "optical" breakwater sheltering those areas behind it from the intrusion of light waves. A careful study of the action of lens diaphragms reveals, however, that a certain amount of the light is bent around their edge and thereby invades that portion where normally no light rays would be expected.

Since the wave length of light is extremely short, the extent to which light rays are bent around a diaphragm is slight, but still is sufficient to affect the quality of the image, particularly when the diaphragm is small. This phenomenon is referred to as *diffraction.* The diffraction pattern produced by a lens is shown in Fig. 73. The center spot represents the legitimate image which would be produced alone were no diffraction present. However, as a result of diffraction, the image is surrounded by a series of concentric rings which gradually fall off in intensity. As the size of the diaphragm is increased, these diffraction rings tend to disappear. However, on the other hand, as the lens is "opened up," other aberrations enter in to impair the quality of the image. Therefore, to secure optimum sharpness, the lens aperture must be small enough to minimize the normal lens aberration and yet not so small as to introduce serious diffraction. For this reason, it is usually found that with a given photographic objective, say, for example, an $f/4.5$ anastigmat, maximum sharpness is secured when operating at some

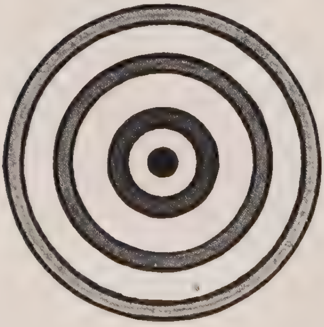
Fig. 73. Diffraction Image of Point.

intermediate aperture such as $f/11$ rather than by stopping down to the smallest possible diaphragm, as for example, $f/32$.

The so-called *resolving power* of a lens may be determined by viewing two closely adjacent point light sources through the lens. As the light sources are brought closer and closer together, a condition arises where they are no longer distinguishable as two separate points of light, and under these conditions the resolving limit of the lens is said to have been obtained. The angle subtended by two such points, which are just far enough apart to permit resolution, is commonly referred to as the resolving power of the lens, or the limit of angular resolution.

When the normal lens aberrations are reduced to such an extent that they do not enter into the consideration of resolving power, and if the rays of light incident upon the lens are parallel, then the angle of resolution in seconds may be determined by the following formula:

$$\alpha = \frac{5}{d}$$

where α = angle of resolution in seconds,
d = diameter of lens, inches.

If other lens aberrations are present, the resolving power will be less than that indicated by the above formula. The phenomenon of diffraction sets a limit to the sharpness of imagery which can be secured from a lens of given size. Beyond this limit, it is impossible to go.

The term "resolving power" is many times used loosely to define the limit of a given photographic objective to record fine detail in an object. When used in this sense, it is of no consequence whether this limit is imposed by diffraction or by lens aberrations.

Diminution in Illumination of the Image with the Distance from the Axis.—Let us now consider the distribution of light intensity over the image area, that is, the decrease in light intensity toward the margins of the image. This effect can easily be seen by exposing a sufficiently large plate toward a white background so that the whole circle of illumination and the falling off in intensity therein appears on the plate. A fair percentage of the decrease in marginal image brilliancy is dependent upon the natural decrease in intensity of extra-axial light, a situation which cannot be avoided by any means of correction. To illustrate, let us designate the intensity of illumination at the center of the image by I_0 and that at the margin by I. According to Lambert's law of photometry $I = I_0 \cos^4 \theta$, where θ is the angle that the marginal ray makes with the optical axis of the lens. In the usual type of photographic objective this angle seldom is greater than 35 to 40 degrees.

It will be observed that this loss increases very rapidly as the angle subtended by the plate at the lens increases. Unfortunately, there is no really practical means to prevent this decrease.

θ	0°	10°	20°	30°	35°	40°
I	100%	94%	78%	56%	45%	34%

In some types of objectives a still further loss of light is incurred by vignetting of the marginal rays by the lens mount itself. In general, this loss of light becomes smaller the closer together the lens elements are placed. Unfortunately, it is not always possible to obtain a maximum aberration correction and at the same time produce a compact lens.

Vignetting of marginal rays by the lens mount, together with the unavoidable decrease in marginal intensity due to the cosine law, may result, in extreme cases, to an intensity of illumination at the margins of from 15 to 25 per cent of the center illumination.

Loss of Light in Lenses.—The speed of a lens is usually denoted by its *f* number which is the ratio between the focal length of the lens and the diameter of its entrance pupil (see page 68). A little thought will reveal, however, that this law is not absolutely valid since it refers to the quantity of light entering the lens and takes no account of the loss of light by absorption in the glass or by reflection at the glass air surfaces. The light lost by absorption is usually negligible since only about two or three per cent of the incident light is lost per centimeter thickness of glass.

The loss of light by reflection is of much greater importance. The magnitude of this loss can be calculated by the equation given by Fresnel which is to be found in any treatise on optics.

PRITSCHOW—The Uneven Light Distribution in the Image Plane of Photographic Objectives. Phot. Ind. **36** (1938) 126, 424.

HRDLICKA—Measuring the Effective Illumination of Photographic Objectives. J. Soc. Mot. Pict. Eng. **14** (1930) 531–533.

MOFFITT—The Light Absorbed by Lenses. Phot. Journal of America **59** (1920) 411.

ODENCRANTS—The Experimental Determination of the Luminosity of Photographic Objectives. Nord Tids. Fot. **9** (1925) 21; Sci. et Ind. Phot. **5** (1925) 87.

ZSCHOKKE—Factors Other than Aperture in the Rapidity of a Lens. Brit. J. Phot. **59** (1912) 823.

Dr. A. Klughardt made such a computation for several photographic objectives, ranging in aperture from *f*/2 to *f*/11. The following table states the results of Dr. Klughardt's computation.[7]

Type	*Lenses*	*Reflecting Surfaces*	*Cemented Surfaces*	*Reflection Loss*	*Total Loss*
Periscope, *f*/11	2	4	—	16%	20%
Dagor, *f*/6.8	6	4	4	18%	22%
Triplet, *f*/3.5	3	6	—	29%	32%
Tessar, *f*/4.5	4	6	1	28%	33%
Dogmar, *f*/6.8	4	8	—	37%	40%
Ernostar, *f*/2.0	6	8	2	38%	48%

It is readily apparent that the magnitude of the reflected light loss increases rapidly with the number of glass surfaces in the lens. It, therefore, follows that an uncemented lens would be slower than a cemented lens having the same relative aperature. To illustrate this, consider the comparison between the Dagor *f*/6.8 and the Dogmar *f*/6.8 as listed in the above table. With the Dagor objective, 78% of the incident light reaches the film, whereas with the Dogmar objective only 60% of the light reaches the film. Hence, the increase in exposure necessary when using the Dogmar would be as 60:78 or 1:1.3. In other words, the exposure with the Dogmar must be 1.3 times that with the Dagor under like conditions.

Methods of treating glass surfaces chemically to reduce the loss of light have been developed by Strong, and by Blodgett,[8] in the laboratories of the General Electric Company and by Cartwright and Turner at the Massachusetts Institute of Technology. The latter method has been applied to lenses for motion picture projection and to several camera lenses.

The Contrast of Photographic Lenses.—Ideally, a photographic objective should be capable of reproducing accurately the full range of brightness in the object photographed. In order to do so, it is

[7] *Photo-Barse* **7** (1925) 414.

[8] Strong, *J. Opt. Soc. Amer.* **26** (1936) 73. Blodgett, *Phys. Review* **51** (1937) 964; **55** (1939) 391. Cartwright and Turner, *Bull. Amer. Phys. Soc.* **13** (1938) No. 10.

Chilton—Light Scatter from Photographic Lenses. Phot. J. **77** (1937) 381.

Roeder—Effect of Light Scatter on Shadow-Detail Rendering and Effective Subject Range. Phot. Ind. **37** (1939) 727.

necessary that each area in the image receive light only from the corresponding area in the object. When other than true image-forming light falls upon the image area, an adulteration of contrast occurs and the photographic reproduction is of lower contrast than that possessed by the original subject.

The factors which most commonly contribute to the presence of extraneous light in the camera are listed below.

Factors Affecting the Contrast of a Lens

1. Camera leaks light.	Avoidable by proper construction and care of the camera.
2. Reflection of light at the glass-air surface of the lens.	Cannot be avoided but can be reduced by proper design of the objective.
3. Reflection of light by bright metallic surfaces of the lens mount, lens diaphragm, and camera interior.	Difficult to control and of rather considerable magnitude.
4. Diffusion of light produced by foreign particles on the glass surfaces. (Finger prints, dust, etc.)	Principally avoidable by keeping the lens clean.
5. Diffusion of light by foreign material within the glass.	Usually of too small a magnitude to be of any practical consequence.

LENS FORMULARY

38

Given Object and Image Distance to determine Focal LENGTH OF LENS:

$$f = \frac{vu}{v + u}$$

Given Object Distance and Focal Length to determine IMAGE DISTANCE:

$$v = \frac{fu}{u - f}$$

Given Image Distance and Focal Length to determine OBJECT DISTANCE:

$$u = \frac{fv}{v - f}$$

JONES AND TUTTLE—Effect of Projection Lens Flare upon the Contrast of a Motion Picture Image. Trans. Soc. Mot. Pict. Eng. **25** (1926) 153–166.

TUTTLE AND WHITE—Factors which Affect the Contrast of a Lens Image in the Motion Picture Camera. Trans. Soc. Mot. Pict. Eng. **11** (1927) 591–599.

RHEDEN—Reflections in Lenses. Phot. Rund. (1921) 101.

FORCH—Reflection Losses at Glass Surface. Phot. Ind. **22** (1936) 612. Brit. J. Phot. **83** (1936) 585.

CHESHIRE—The Loss of Light in Lenses. Brit. J. Phot. **59** (1912) 597, 645.

NUTTING—The Brightness of Optical Images. Phot. J. **54** (1914) 187.

Given Image and Object Distances to determine MAGNIFICATION:

$$m = \frac{v}{u} = \frac{f}{u - f}$$

Given Magnification and Focal Length to determine IMAGE DISTANCE:

$$v = \left(\frac{m + 1}{m}\right) f$$

Given Magnification and Focal Length to determine OBJECT DISTANCE:

$$u = (m + 1)f$$

Relations between Image Distance, Object Distance, and Focal Length:

$$\frac{1}{u} + \frac{1}{v} = \frac{1}{f}$$

$$f^2 = (v - f)(u - f)$$

Diameter of Permissible Circle of Confusion (inches):

$$d = \frac{f}{1000}, \text{ where } f = \text{focal length in inches.}$$

Hyperfocal Distance:

$$H = \frac{f^2}{(f/\text{number})d}$$

Distance from Lens to Nearest Point in Focus:

$$L_N = \frac{Hu}{H + (u - f)}$$

Distance from Lens to Farthest Point in Focus:

$$L_F = \frac{Hu}{H - (u - f)}$$

Total Depth of Field $= (L_F - L_N)$

Given Focal Length and f/number of Lens to determine Diameter of Entrance Pupil:

$$E' = \frac{f}{f/\text{number}}$$

Factor by which to Multiply Exposure to Compensate for Extending the Lens beyond the Infinity Position:

$$x = \frac{v^2}{f^2}$$

Distance by which Lens must be Moved from its Infinity Position to focus upon any desired object distance (Helpful in checking footage scale on camera bed).

$$\Delta v = \frac{f^2}{f - u}$$

Formula for the Focal Length of a Thin Lens:

$$\frac{1}{f} = (n - 1)\left(\frac{1}{R_2} - \frac{1}{R_2}\right)$$

Dioptric Power of a Lens: f in c.m

$$D = \frac{1}{f}, \text{ where } f = \text{focal length in meters} \quad ; \; f = \frac{1}{D}$$

Formula for the Focal Length of a Thick Lens:

$$\frac{1}{f} = (n - 1)\left(\frac{1}{R_1} - \frac{1}{R_2} + \frac{(n - 1)t}{nR_1R_2}\right)$$

Equivalent Focal Length of Two Coaxial Thin Lenses which are Separated by a Distance a.

$$f = \frac{f_1 f_2}{f_1 + f_2 - a}$$

The following notation is used in the above formulas:

f = focal length of lens.
u = distance from lens to subject, inches.
Δv = distance from lens to negative plane, inches.
m = linear magnification.
d = diameter of the maximum permissible circle of confusion, inches.
H = hyperfocal distance, inches.
L_N = distance from lens to nearest point in focus, inches.
L_F = distance from lens to farthest point in focus, inches.
E = diameter of the entrance pupil of the lens, i.e., the image of the stop as produced by the optics in front of the stop, inches.
x = exposure correction factor.
v = distance that lens must be moved from its infinity position to produce sharp focus for an object distance u, inches.
n = index of refraction of the lens material.
R_1 = radius of the front lens surface, inches.
R_2 = radius of the rear lens surface, inches.
D = dioptric power of a lens, diopters.
t = thickness of the lens, inches.

Exposure Correction Required When Lens is Not at Infinity Position.—The f/numbers marked on the lens mount of any camera indicate the relative light gathering power of the lens for the case where the lens is set at infinity, i.e., when $v = f$. For other lens positions, as for example, when one is photographing at an object distance of 6 feet, the f/numbers as marked are incorrect, and therefore an exposure correction should be made to compensate for this error. The amount by which the exposure should be corrected for this condition given by the ratio v^2/f^2. To illustrate the use of this relation, consider the case where the lens has been racked forward from its infinity position by an amount equal to one focal length, as would be the case for copying at unit magnification. Under these conditions,

$$v = 2f, \text{ hence } \frac{v^2}{f^2} = \frac{(2f)^2}{f^2} = 4.$$

This indicates that four times the exposure is needed at unit magnification than would be required when the lens is at the infinity position. Hence, if a photoelectric exposure meter indicated the exposure to be one second at f/16, it would be necessary at unit magnification to give either 4 seconds at f/16 or to open the lens up to f/5.6 if the exposure time is kept at one second.

Since this correction is tedious to calculate in the field, a table relating magnification with exposure correction is given below:

Magnification	*Exposure Factor*	*Magnification*	*Exposure Factor*
1/30	1.07	7	64
1/20	1.10	8	81
1/10	1.21	9	100
1/8	1.27	10	121
1/6	1.36	11	144
1/4	1.56	12	169
1/2	2.25	13	196
3/4	3.06	14	225
1	4	15	256
2	9	16	289
3	16	17	324
4	25	18	361
5	36	19	400
6	49	20	441

McILWAINE—Calculating Exposures for Close-Ups. Phot.Tech. **1** (1939) Nov. p. 44.

MARTIN—A Scale for Indicating the Increase in Exposure When the Bellows is Extended. Amer. Phot.

WHEELER—Chart for Lens Calculations. Phot.Tech. **2** (1940) Feb. p. 31

CHARLES—Determination of Exposures in Copying by Artificial Light. Brit. J. Phot. **69** (1922) 709.

CHAPTER III

PHOTOGRAPHIC OBJECTIVES

Introduction.—This chapter is designed to provide a concise summary of the principal types of photographic objectives in use today. No attempt has been made to make it exhaustive, nor to include constructional details which would be of interest only to the designing optician. A bibliography and full patent data have been included which it is believed will meet the needs of those requiring more extended and detailed information.

Single Lenses.—Single uncorrected lenses are seldom used today except on the very cheapest cameras. A single lens cannot be corrected in any way and consequently sharp definition can be obtained only with a small diaphragm. As the visual and photographic images do not coincide, the single lens is suitable only for box cameras or those focused by scale.

The meniscus form is usually employed since it has a larger useful field than a biconvex lens (Fig. 74).

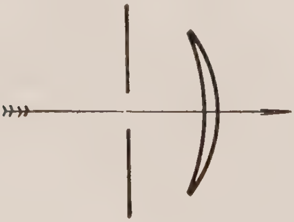

Fig. 74.

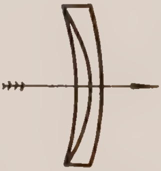

Fig. 75.

The usual form of single achromatic lens consists of two cemented menisci, the positive (Fig. 75) lens being next to the diaphragm and consisting of crown glass while the rear lens is negative (dispersing) and consists of flint glass. This construction appears to be due to the English optician Grubb[1] and results in better spherical correction and a larger field than the combination of a biconcave and biconvex element used in the earlier single lenses of Chevalier (Fig. 76).

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[1] B.P. 1968 of 1857.

The three-glass design patented by Dallmeyer (Fig. 77) is not used today despite its larger aperture because of the increased cost of manufacture.

On some box, and other fixed focus cameras, provision for photographing nearby objects is made by mounting a simple negative or positive lens of low power in front of the diaphragm in such a way that it can be readily shifted to one side when not required. If the front lens is negative, it is removed and the rear lens used alone when photographing nearby subjects. With a low power positive lens, these conditions are reversed and the front lens is used only for nearby subjects.

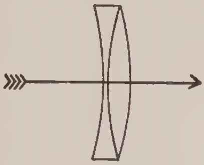

FIG. 76.

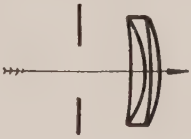

FIG. 77.

Double Objectives.—Simple double objectives of the type shown in Fig. 78 are used frequently where an inexpensive lens having a larger aperture than a single lens is desired. This construction results in a lens free from distortion, a flatter field and better spherical correction than the simple meniscus lens. The relative aperture is usually about $f/11$.

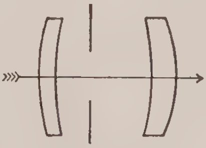

FIG. 78.

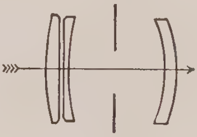

FIG. 79.

A modification of the simple doublet is shown in Fig. 79. In this, the front element consists of a positive and negative component, the distance between the two being adjustable at will. The focal length of the complete lens depends upon the separation of the two components of the front element; thus the lens may be focused by screwing the front element of the lens in or out so as to vary the separation between the two.

Soft-Focus Lenses.—Lenses corrected partially for spherical or chromatic aberration in order to produce a diffused or "soft-focus" image are used frequently by pictorialists who object to the sharp definition of a fully corrected lens.

In most cases, the objectives are corrected for chromatic but not completely for spherical aberration; the undercorrection of the latter results in the diffused image characteristic of such lenses. Objectives of this type take several constructional forms. A number are single lenses. *The Plastigmat* of Bausch & Lomb and the *Verito* of Wollensak (Fig. 80) are of unsymmetrical construction, the front component consisting of a single lens and the rear a cemented doublet resembling a single landscape lens. In the case of the Verito, the single element may be used alone, thus obtaining a focal length approximately twice that of the complete lens. Both lenses are corrected for chromatic aberration and there is no focus difference. The degree of diffusion is controlled by the diaphragm.

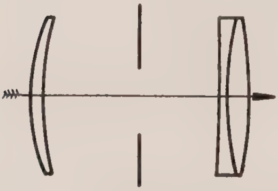

Fig. 80.

In a number of cases, anastigmatic lenses intended particularly for portrait work and Petzval-type portrait lenses are designed in such a way that a diffused image may be obtained when desired by altering the position of one of the elements of the lens.

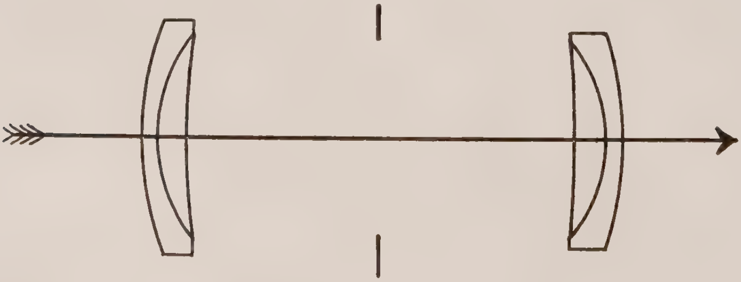

Fig. 81. The *Aplanat* of Steinheil and *Rapid Rectlinear* of Dallmeyer.

The Rapid Rectilinear or Aplanat.—Historically, this objective is interesting as the first well corrected symmetrical[2] lens covering a wide field at a comparatively large aperture. It has, however, been almost completely supplanted in recent years by anastigmatic lenses of the simpler constructions, since these are no more difficult to manufacture and possess an astigmatically flattened field with superior definition and, frequently, a larger aperture.

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[2] A double objective in which the arrangement of glasses is the same on both sides of the diaphragm is said to be of symmetrical design. Such objectives are usually so designed that the front and rear components may be used separately at smaller apertures. In this case, the complete objective affords a choice of at least two and frequently three focal lengths when the single elements are used.

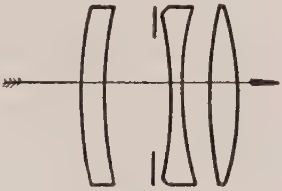

FIG. 82.

Triplet Constructions (Not Anastigmatic).—Simple triplet constructions are used for several objectives designed for studio portraiture. Usually no attempt is made to secure a high degree of correction in such cases; the aberrational errors remaining, are so controlled as to produce a "plastic" image. The *Sigmar* ($f/4$) of Bausch & Lomb, and the *Hypar* of Goerz ($f/3.5$) are of this type. The character of the image is intermediate between that of fully corrected and soft focus lenses.

Conditions Necessary for the Simultaneous Correction of Astigmatism and Spherical Aberration.—The conditions necessary for the simultaneous correction of astigmatism and spherical aberrations have been summarized by R. Steinheil as follows:[3]

"An objective may be corrected for spherical aberration if two media are separated by a convex surface turned towards the medium of higher refraction; for astigmatism if the surface is concave to the medium having the higher refraction."

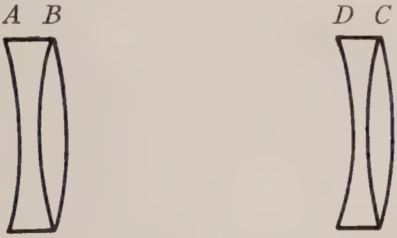

FIG. 83. Illustrating the Conditions Necessary for the Correction of Spherical Aberration and Astigmatism in a Cemented Doublet Lens.

Thus, in Fig. 83, *A* and *C* are flint glass lenses of high relative dispersion and *B* and *D* are of crown glass with low dispersion. In the lens at the left, the cemented surface is convex to the medium of higher refraction, thus correcting for spherical aberration, while in the lens at the right, the cemented surface is concave to the glass having the higher refraction, the condition necessary for the removal of astigmatism.

Simultaneous correction for both spherical aberration and astigmatism, therefore, involves the employment of one or more surfaces, which may or may not be cemented surfaces, concave to media having a higher refractive index and other surfaces convex to media with a higher refractive index.

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[3] *Eder's Jahrbuch,* 1897. "Origin and History of the Orthostigmats."

After the introduction of Jena glass, it became possible to make the collecting lens of glass having higher refraction and lower dispersion than the dispersing lens and thus secure astigmatic correction. The old achromat made of ordinary crown and flint could be corrected spherically but not astigmatically; the new achromat, while corrected astigmatically, cannot be spherically corrected. However, by combining the ordinary crown and flint of the old achromat with the barium crown glass of the new achromat, it became possible to correct both astigmatism and spherical aberration in the same lens. By combining two such achromats both of which are individually corrected to form a symmetrical objective, a larger aperture becomes possible together with correction for curvature of field, coma, and distortion. This is the principle followed in the construction of most of the symmetrical lenses as the Goerz *Double Anastigmat* or *Dagor,* the Voightlander *Collinear,* Turner-Reich Anastigmat, etc. The other method is to use two dissimilar combinations, one of which is spherically corrected while the other is astigmatically corrected; the two when placed on opposite sides of the diaphgram form an unsymmetrical objective which is completely corrected as a whole but not individually. This is the principle followed in the construction of most of the large aperture anastigmats.[4]

Objectives Composed of Three Cemented Lenses.—The conditions necessary for the correction of both astigmatism and spherical correction may be satisfied in a single objective consisting of three cemented lenses. Such an objective may take several forms (Fig. 84).

TYPE A

In the construction shown at the left, the indices of refraction of the three glasses increase from left to right, i.e., in the direction of the incident light. Hence, the first cemented surface is convex to the glass of lower refraction, meeting the condition for the correction of spherical aberration. The second cemented surface is convex to the glass of higher refraction and thus satisfies the requirement for astigmatic correction. Consequently, correction for both is secured by the opposition of the two cemented surfaces in an objective composed of only three cemented lenses.

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[4] The statement is often made that anastigmatically corrected objectives were not possible until after the introduction of Jena glass. This is not true. The Steinheil *Unofocal* and the *Omnar* of Busch do not require any of the glasses developed at Jena and the Cooke triplet can be made with the older glass. It is true, however, that designers were unable to produce an astigmatically corrected objective until the new glasses of Schott at Jena became available.

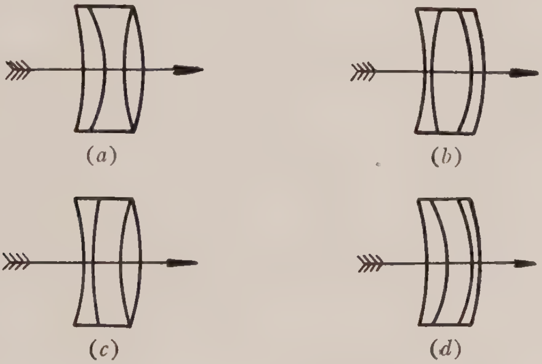
(*a*) (*b*) (*c*) (*d*)

FIG. 84. Constructional Forms of Anastigmatic Objectives Composed of Three Cemented Lenses.

Well designed objectives of this type give satisfactory definition at an aperture of about *f*/12.5. The combination of two such objectives on opposite sides of the diaphragm to produce a symmetrical objective enables the aperture to be increased to *f*/6.8, or even larger, if the complete objective is designed to cover a somewhat smaller field.

This construction is especially noteworthy for the excellent definition of both the single and complete objective and for the comparatively wide angle (70–80°) covered sharply by the double objective, particularly at a small stop.

Both Paul Rudolph of the firm of Carl Zeiss, and Von Hoegh of the firm of C. P. Goerz, applied for patents on lenses of this type at about the same time.[5] The first objective of this type to be placed on the market, however, was the *Dagor* of Goerz (Berlin).

The following objectives are of this type:

Aristostigmat, *f*/6.8	Hugo Meyer & Company—Goerlitz (Germany)
Symmar, *f*/6.8	Joseph Schneider & Company—Kreuznach (Germany)
Double Orthar, *f*/6.8	Plaubel

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[5] Rudolph, B.P. 4692 of 1893. Von Hoegh, D.R.P. 74,437 of 1892; B.P. 23,378 of 1892.

In 1908, Zschokke of the firm of C. P. Goerz improved the astigmatic correction of lenses of this type through the use of newer glasses of higher refractive index for the central dispersing lens.[6] A similar improvement was patented also by Carl Zeiss.[7]

TYPE B

The construction shown in (*b*) of Fig. 84 consists of two negative lenses, one having a lower, the other a higher refractive index than the interposed positive lens. In this case, the arrangement of cemented surfaces is reversed and the indices of refraction decrease in the direction of the incident light.

This construction was patented by Rudolph for Carl Zeiss in 1892[8] and an objective of this type has been made for several years by Steinheil as the *Satz-Anastigmat* and by Watson of London as the *Holostigmat.* The single elements of this have a relative aperture of *f*/8.5 and the double lens, formed of two like halves, an aperture of *f*/4.6.

The outer meniscus lenses of this design permit the attainment of a particularly favorable proportion between the diameter of the lenses and the length of the objective, together with a relatively large aperture, making this construction especially suitable for wide angle objectives. The *Angulon* of Joseph Schneider (Kreuznach, Germany) designed by Tronnier has a relative aperture of *f*/6.8 (as a double objective) and covers an angle of 100° (Fig. 85).[9]

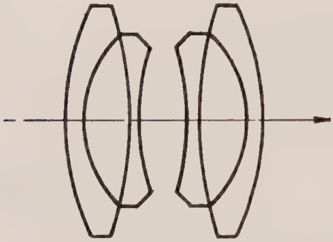

FIG. 85.

TYPE C

The construction shown in (*c*) of Fig. 84 consists of a meniscus lens of low refraction between a double convex positive lens of high refractive index and a double concave negative lens of medium refraction. The Voightlander *Collinear*[10] and the Steinheil *Orthostigmat* are the best known objectives of this type.

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[6] B.P. 13,902 of 1908.

[7] B.P. 26,317 of 1910.

[8] B.P. 4692.

[9] U.S.P. 1,882,530 of 1932.

[10] B.P. 562,614 of 1896.

Type D

A fourth design consists of three menisci, the two nearest the diaphragm being positive, the third negative, or dispersing. The central meniscus is composed of glass of low refractive index, the rear of higher index, while the lens nearest the diaphragm is of glass with the highest refractive index of all. This design is favorable for the construction of spherical aberration, but does not result in the same degree of astigmatic correction as the other designs. This design was patented by Kaempfer for Voightlander in 1896.[11]

Objectives Composed of Four Cemented Lenses.—This design represents the combination of the old achromat and the new achromat, made possible by the glasses produced at Jena, which enabled the astigmatic correction to be made.

This construction, because of the increased number of surfaces at the disposal of the designer, is especially noteworthy for the high degree of correction and the large flat field, but is not suitable for large aperture objectives.

Some of the forms given the four glass cemented element are shown in Fig. 86.

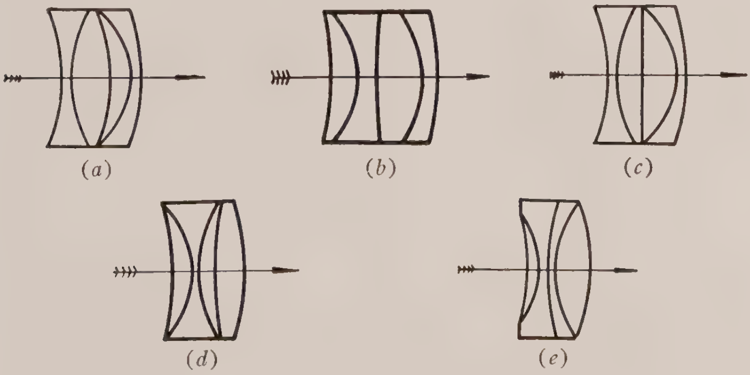

Fig. 86. Constructional Forms of Anastigmatic Objectives Composed of Four Cemented Lenses.

The design shown in (*a*) was calculated by Paul Rudolph and introduced by Carl Zeiss of Jena as the *Protar*.[12]

The single elements have a relative aperture of *f*/12.5 and the double lens, composed of two such elements, an aperture of *f*/6.8 or *f* 7.7, depending upon the relative focal lengths of the two components. A lens of similar design introduced by Ross Ltd. of London (England), from calculations by Hasselkus, as the *Combinable*,[13] has a relative aperture of *f* 11 for the single elements and *f*/5.5 for the double objective.

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[11] B.P. 562,614 of 1896.

[12] B.P. 4692 of 1893. The following patents relate to objectives of this type: Rudolph (Carl Zeiss) D.R.P. 228,677; B.P. 23,607 of 1909.

The design shown in (*b*) was patented by Carl Zeiss from calculations by Merté[14] and has a relative aperture of *f*/9.5 for the single elements and *f*/4.5 for the double objective.

The constructions shown in (*c*), (*d*) and (*e*) of Fig. 86 are all of minor importance. The first of these three was used in a lens introduced by Goerz as the *Pantar*.[15] The second form was introduced by Reichert in Vienna as the *Combinar* and the third by Rietzschel as the *Linear*.[16] None of these lenses are now made.

The Five Lens Element.—The five lens element increases the number of surfaces and elements of construction at the disposal of the calculator and makes possible an exceptional degree of correction for the single element. Despite this, the five lens element has never been popular and but few opticians have placed lenses of this design upon the market. The construction shown in (*a*) of Fig. 87 was introduced by the Gundlach-Manhattan Optical Company of Rochester, N. Y. as the *Turner-Reich* lens. Another lens of this type (*b* of Fig. 87) was introduced by Goerz from calculations by Von Hoegh.

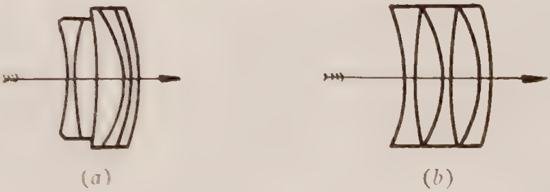

FIG. 87. Constructional Forms of Anastigmatic Objectives Composed of Five Cemented Lenses.

Objectives Developed from the Three and Four Glass Cemented Lenses.—In a cemented element of three lenses, anastigmatic flatness is obtained and spherical aberration corrected by the use of two cemented surfaces, one of which is collective, the other dispersive in effect. If, in computation, the necessary power of refraction of the central lens is reduced until it becomes equal to that of air, an element of two glasses is produced which satisfies the conditions necessary for the correction of spherical aberration and astigmatism, since one surface is concave to a medium having a lower refractive index, namely, air, while the other is convex. Objectives of this type were introduced by Goerz, from calculations by Von Hoegh, as the *Celor* and *Syntor;* the first with a maximum aperture of $f/4.5$ and the latter, designed for hand camera use, with an aperture of $f/6.8$. With this construction, however, full comatic correction is impossible unless the symmetrical design is departed from, and the Celor and Syntor are no longer made.

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[13] B.P. 29,639 of 1913.

[14] U.S.P. 1,479,197 and 1,479,196 of 1924; B.P. 146,465 of 1919.

[15] D.R.P. 171,369 of 1904.

[16] D.R.P. 118,466 of 1898.

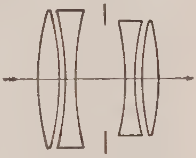
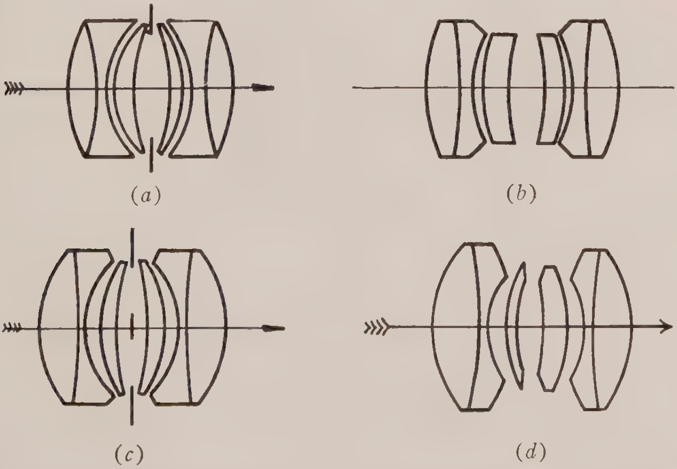


FIG. 88. Objective Developed from the Three-Glass Cemented Lens. The *Celor* of Goerz.

A later introduction, known as the *Dogmar,* in which the symmetrical construction has been departed from, is still made. It has an aperture of $f/4.5$ and the single elements may be used alone at $f/32$.

Objectives of the type illustrated in Fig. 89 may be regarded as a development of the three glass cemented element, one of the three lenses being separated from the remaining two by an air space. The greater freedom which this construction affords the designer makes



(*a*) (*b*)

(*c*) (*d*)

FIG. 89. Development of the Three-Glass Element Through the Introduction of Air-Spaces.

possible an increase in the relative aperture without materially reducing the angular field covered or the degree of correction.

The design shown in (*a*) has been manufactured for several years by Hugo Meyer of Gorlitz (Germany) as the *Euryplan*.[17] The single lenses have a relative aperture of *f* 11 and the double objective an aperture of *f* 6. The Zeiss *Orthometar*,[18] (*b*), designed for aerial photography, has a relative aperture of *f* 4.5 and covers an angular field of 65°.

The *Double Plasmat* introduced by Hugo Meyer (Goerlitz, Germany) from calculations by Paul Rudolph (*c*) has been designed primarily to obtain greater depth of plasticity on planes before and behind the plane in sharp focus. The single lenses have a relative aperture of *f*/8 and the double objective *f*/4.5.

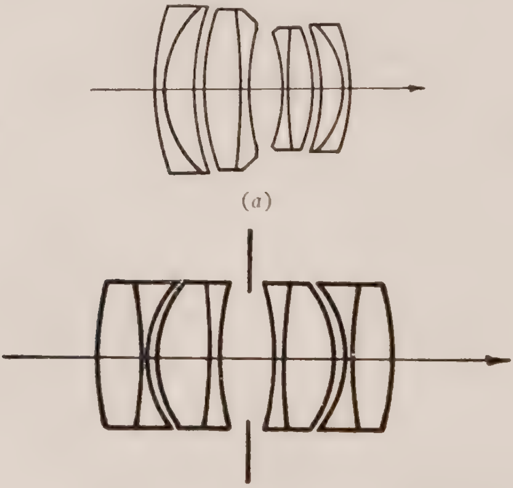


FIG. 90. Objectives Developed from the Four-Glass Cemented Lens Through the Introduction of Air-Spaces.

The Ross *Wide Angle X-Press* (*d*) is also designed primarily for aerial photography and includes an angle of 80° at a relative aperture

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[17] G.P. 135,742.

[18] B.P. 278,338.

KINGSLAKE—Design of Wide-Aperture Photographic Objectives. J. Appl. Physics **11** (1940) 56.

LEE—New Lens Systems. Phys. Soc. Reports on Progress in Physics **7** (1940) 130.

of $f/4$. The single elements, however, are not designed for use alone.

The objective shown in Fig. 90 may be regarded as a development of the four glass cemented element, an air space being added to afford the designer greater liberty in meeting the conditions necessary for adequate correction. The Cooke (Taylor, Taylor and Hobson, Leicester, England) Convertible Series XV[19] is noted for its excellent correction for color. The single lenses have a relative aperture of $f/11$ and the double lens an aperture of $f/6.8$.

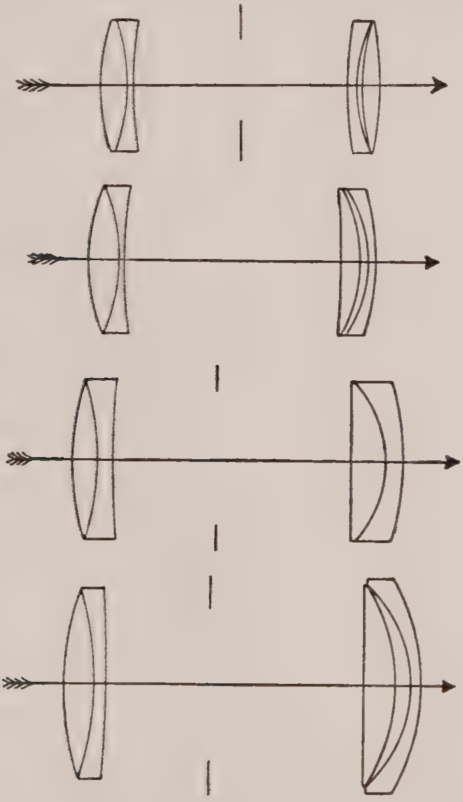

Fig. 91. Petzval's Portrait Objective and Its Modifications.

The Wollensak *Velostigmat* Series I (Wollensak Optical Company, Rochester, N. Y.) is similar.

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[19] B.P. 376,044 of 1932.

The design shown in (*b*) was calculated by Warmisham (Taylor, Taylor and Hobson Ltd., Leicester, England) but was not placed upon the market.[20] It had a relative aperture of *f*/4.5 for an angular field of 80°.

Lenses Based Upon the Portrait Lens of Petzval.—The tremendous contribution of Joseph Petzval to photography, and particularly portrait photography, through the calculation of the portrait objective known as the Petzval lens, has already been noted. (Page 10.) The original Petzval design (Fig. 91) consisted of a cemented biconvex and biconcave lens in front of the diaphragm and a rear component of two separate lenses, the first a negative meniscus with its convex side facing the diaphragm, and a double covex collecting, or positive, lens, the air space acting as a negative meniscus lens. This design results in excellent definition but only for a small angular field (about 24°), which is decidedly curved and, owing to the length of the objective, the illumination is uneven diminishing rapidly from the center towards the edges. Practically, lenses of this type are suitable only for head and shoulder portraiture, or for work requiring a small angular field.

Portrait lenses of the Petzval type are still popular although they are gradually being superseded, even for portraiture, by anastigmatic objectives. Most of the Petzval type lenses made in recent years appear to be based on the modified form patented by J. H. Dallmeyer of London in 1866. The modification consisted essentially in reversing the two lenses of the rear half of the lens and had the effect of increasing slightly the angular field and permitted the use of a somewhat larger aperture. Other modifications were made by Voightlander in 1878, who was able to remove the air space in the rear element at some sacrifice of the spherical correction and by Zincke-Sommer (1870) who increased the aperture to *f*/2.3.

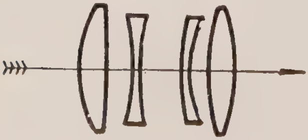

FIG. 92.

The Petzval construction, because of its excellent central definition, has continued to find favor with calculators for projection lenses and for photographic purposes, where a large aperture is required and the field to be covered is small, as in cinematography.

Urban of Berlin in 1921 increased the speed to *f*/2.0 with acceptable correction for a field of 25° by introducing air spaces in both the front and rear elements (Fig. 92) and through the use of newer glasses, in particular a heavy baryta crown.[21] A similar design was patented by Frederick and Altman (Fig. 93), Eastman Kodak Company.[22] In both of these designs, the vignetting of the marginal portions of the image has been greatly improved over earlier designs of this type.

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[20] B.P. 260,801 of 1925.

Lee (Taylor, Taylor and Hobson, Leicester, England) replaced the front half of the Petzval design with a triplet to obtain a relative aperture of *f*/1.8 and a comparatively flat field of about 35°.[23]

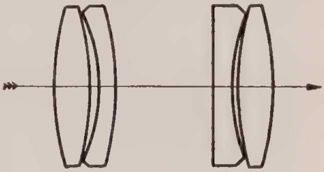

Fig. 93.

Warmisham also of Taylor, Taylor and Hobson patented three designs (Fig. 94) in the first of which the front member consists of two converging members separated by an air space with a dispersing effect. In the second, the rear element is divided, a positive meniscus being added to the usual rear half. The third consists of a combination of the modified front and rear halves together. This results in comparatively good definition at a relative aperture of *f*/1.5.[24]

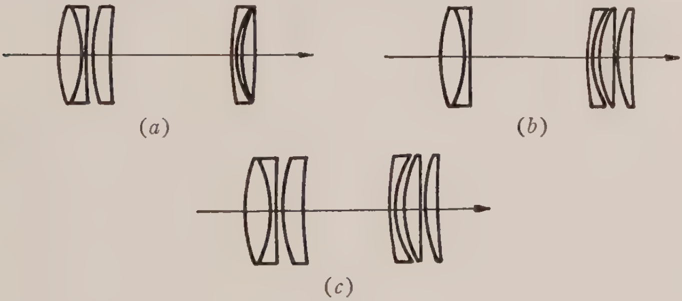

Fig. 94.

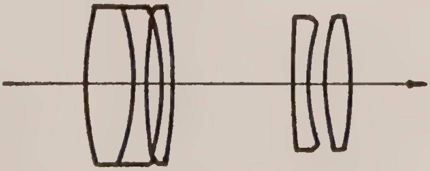

Fig. 95.

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[21] U.S.P. 1,474,743 of 1923.
[22] U.S.P. 1,620,337 of 1927.
[23] B.P. 299,983 of 1927.
[24] B.P. 258,092 of 1925; U.S.P. 1,797,202 of 1931.

Two further designs patented by Schade[25] (Eastman Kodak Company) (Fig. 95) are designed primarily for projection purposes and have a relative aperture of f/1.3, with a greatly improved correction for coma and spherical aberration and a considerable reduction in curvature of field and astigmatism.

The Anastigmat Triplet of H. D. Taylor and Its Derivatives.—The first successful anastigmatic triplet objective was developed by H. D. Taylor[26] in 1893, and is frequently termed the *Cooke* triplet, since Mr. Taylor was then in the employ of T. Cooke and Sons, Ltd.

In this triplet construction (Fig. 96), the two outer collecting lenses are identical and are designed to be practically free from coma; this result is secured by the use of an intermediate form of lens in which the inward coma of one surface is neutralized by the outward coma of the opposite surface. The burden of correcting the entire system is thrown upon the central dispersing lens, which fulfills a threefold office: (1) It flattens the final image and corrects marginal astigmatism, producing a flat astigmatic field; (2) It corrects the color aberrations of the convergent lenses and makes the complete system achromatic; (3) It corrects the residual spherical aberration of the two collecting lenses and renders the final image aplanatic.

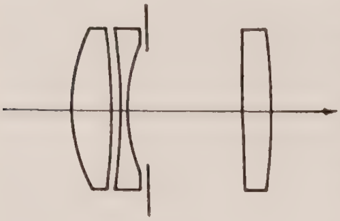

FIG. 96.

Despite its extreme simplicity, the triplet of H. D. Taylor results in excellent performance and lenses based upon his patents were placed upon the market by Taylor, Taylor and Hobson, Ltd., of Leicester (England) in several series from f/8 to f/3.5, the latter being designed for portrait work and covering a smaller angular field than the others.[27]

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[25] U.S.P. 2,158,201 and 2,158,202 of 1939.

[26] B.P. 22,607.

[27] The following patents relate to photographic objectives based upon the simple triplet design of H. D. Taylor:

Lee, Taylor, Taylor and Hobson, B.P. 155,640 of 1919. An unsymmetrical triplet with improved correction and a flat field of 45° at $f/3.0$.

Tronnier, Schneider-Werke, U.S.P. 1,987,878 of 1935. An unsymmetrical triplet with improved correction for an aperture of $f/4.5$.

Warmisham, Taylor, Taylor and Hobson, B.P. 157,036 of 1920. A triplet with shallower curves to reduce manufacturing costs.

Among other lenses employing a similar triplet construction may be mentioned:

Apotar, *f*/4.5	Agfa—Frankfort (Germany)
Aldis, Series O, *f*/3.0	Aldis Bros.—Birmingham (England)
Topaz, *f*/2.9, *f*/3.5, *f*/4.5, *f*/6.3	Boyer Etab.—Paris (France)
Glaukar, *f*/2.5, *f*/2.8, *f*/3.1, *f*/4.5	E. Busch & Co.—Rathenow (Germany)
Trioplan, *f*/3	Hugo Meyer—Goerlitz (Germany)
Portrait-Trioplan, *f*/3.0	Hugo Meyer—Goerlitz (Germany)
Trioplan, *f*/2.9 *f*/4.5 *f*/6.3	Hugo Meyer—Goerlitz (Germany)
Eurygon, *f*/4.5	G. Rodenstock—Munich (Germany)
Eurynar, *f*/3.5, *f*/4.5	G. Rodenstock—Munich (Germany)
Trinar, *f*/2.9, *f*/4.5, *f*/6.3	G. Rodenstock—Munich (Germany)
Trylor, *f*/4.5, *f*/6.3	H. R. Roussel—Paris (France)
Radionar, *f*/2.9, *f*/3.5, *f*/4.5, *f*/6.3	Joseph Schneider & Company—Kreuznach (Germany)
Kinoplan,	Schneider-Werke—Kreuznach (Germany)
Radionar, *f*/6.3	Schneider-Werke—Kreuznach (Germany)
Cassar, *f*/4.5 and *f*/3.5	Steinheil and Soehne—Munich (Germany)
Cassar, *f*/2.5, *f*/4.8	C. A. Steinheil & Soehne—Munich (Germany)
Triplar, *f*/2.8	C. A. Steinheil & Soehne—Munich (Germany)
Helomar, *f*/3.5	Voightlaender & Soehne—Brunswick (Germany)
Voigter, *f*/3.5, *f*/7.7	
Supar, *f*/3.5, *f*/4.5	Wray Ltd.—Bromley (England)
Triotar, *f*/3 and *f*/3.5	Carl Zeiss—Jena (Germany)
Triotar, *f*/3.5, *f*/4.5, *f*/5.6	Carl Zeiss—Jena (Germany)
Triplet, *f*/4.8	
Nettar, *f*/3.5, *f*/7.7	Zeiss Ikon—Dresden (Germany)
Novar, *f*/6.3	

Objectives Developed from the Triplet Design of H. D. Taylor.—The simple triplet of Taylor was modified by H. L. Aldis (B.P. 5170) who cemented the central dispersing lens to the front collecting lens, placing a single collecting lens in the rear of the diagram (Fig. 97). In this design, the spherical corrections are made principally by the cemented surface and astigmatic flattening of the field by the rear element. This construction is simple and well adapted to objectives of moderate aperture; i.e., *f*/7.7 to *f*/6.3.

A second development of the original simple triplet of H. D. Taylor consists (Fig. 98) of two positive elements, each a cemented doublet, with a centrally placed negative component. The increase in the number of elements of construction and the introduction of cemented surfaces enable the necessary corrections to be carried out more easily and completely than in the simple triplet and results in an objective with better correction and covering a larger field.

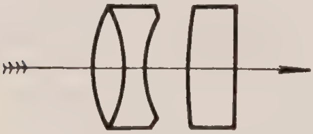

Fig. 97.

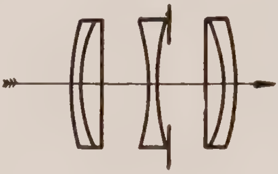

Fig. 98.

Both symmetrical and unsymmetrical objectives of this type have been designed. The unsymmetrical design permits more complete correction for astigmatism and curvature of field, but is not perfectly rectilinear.

The best known objective of this type is the *Heliar* of Voightlander (Brunswick, Germany) which was calculated by Harting (U.S.P. 716,035). This has been made in several series with apertures up to *f*/3.5. An objective of similar design, known as the Dynar, with an aperture of *f*/6.8 is no longer made.

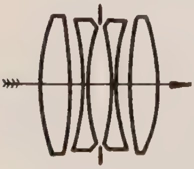

Fig. 99.

A third modification of the simple triplet consists essentially in dividing the central negative lens into two similar lenses but of lower individual power. This permits the employment of shallower curves than the single negative lens of the original triplet, and enables the corrections for coma to be carried out more thoroughly, resulting in a larger flat field. The best known objective of this type is the *Aviar* of Taylor, Taylor and Hobson which was designed by Warmisham (Fig. 99).[28]

The demand, in recent years, for large aperture objectives for cinematography and the miniature camera has caused designers to give particular attention to the possibilities of the triplet construction with the result that a large number of patents have been issued for lenses which have been derived from one of the designs already described, although in their final form many of these developments bear little or no resemblance to the triplet. Since few of these designs have actually been used, detailed discussion seems unnecessary. In Fig. 100 are shown a number of designs patented by Lee and Warmisham, who are associated with Taylor, Taylor and Hobson of Leicester (England), and Bertele

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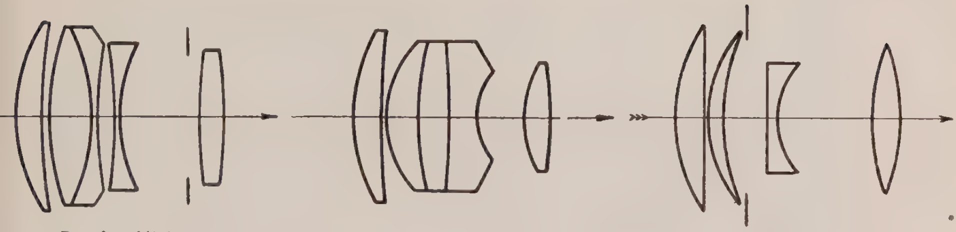
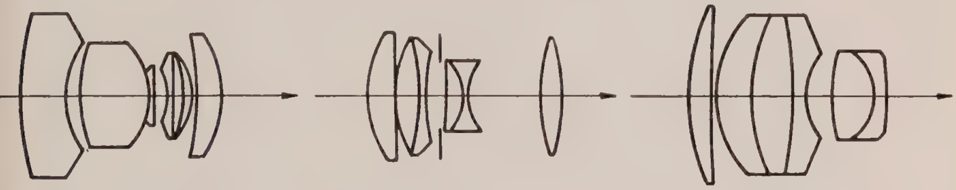
[28] B.P. 113,590 of 1918 and B.P. 312,536 of 1929.



Bertele: *f*/2.9
B.P. 237,861 (1925)

Bertele: *f*/1.2
U.S.P. 2,141,733 (1937)

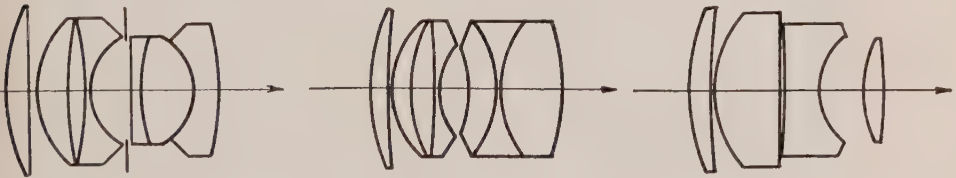
Bertele: *f*/2
B.P. 186,917 (1923)



Bertele: *f*/2.7 (*Biogon*)
U.S.P. 2,084,309 (1937)

Bertele
B.P. 234,743 (1924)

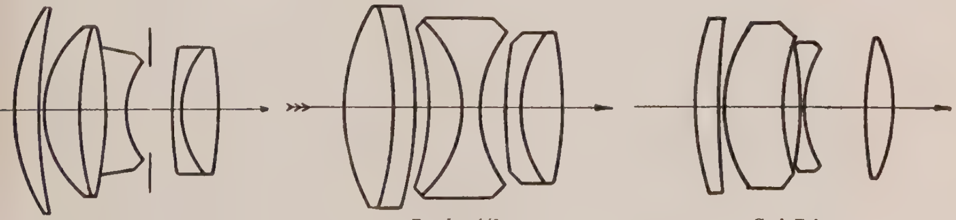
Bertele: *f*/1.4
U.S.P. 2,029,806 (1935)



Bertele: *f*/1.5 (*Sonnar*)
U.S.P. 1,975,678 (1934)

Bertele:
B.P. 499,290 (1938)

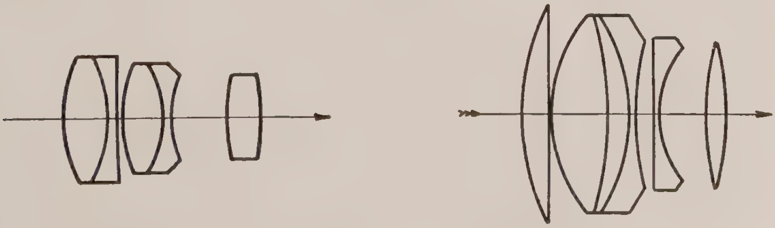
Lee: *f*/1.4
B.P. 477,424



Bertele: *f*/2
B.P. 383,591 (1932)

Berek: *f*/2
U.S.P. 1,939,098

Carl Zeiss
B.P. 496,865



Warmisham: *f*/1.8
B.P. 280,392

Belicke: *f*/2 (*Ernostar*)
B.P. 186,917 (1921);
191,702 (1922);
193,376 (1923);
232,531 (1924)

FIG. 100. Large-Aperture Anastigmat Lens Constructions Developed from the Cooke Triplet.

who was formerly in the employ of the Erneman-Werke of Dresden, but later a member of the staff of Carl Zeiss of Jena (Germany).

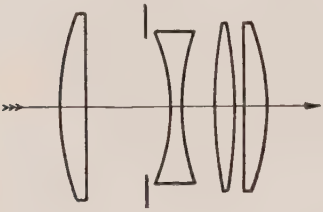


Fig. 101.

The *Ernostar* with an aperture of *f*/2 was placed on the market by the Erneman-Werke of Dresden, but is no longer made. The *Sonnar* has a relative aperture of *f*/1.5 and is designed for use on the Zeiss *Contax*.

A design, patented by Belicke[29] in which the rear collecting lens of the triplet is divided into two, is shown in Fig. 101.

Triplets with Cemented Rear Doublet.—The first triplet of this type was designed by Paul Rudolph and issued commercially by Carl Zeiss of Jena (Germany) in 1903 as the *Tessar* (Fig. 102).

The Tessar was not derived from the triplet of H. D. Taylor, however, but from two earlier lenses designed by Rudolph. One of these (Fig. 103) consisted of a spherically corrected glass pair and an astigmatically corrected glass pair on opposite sides of the diaphragm. This design was placed on the market as the *Protar* (not to be confused with later lenses bearing the same name) by Carl Zeiss in 1890, and while it was excellently corrected for a large angular field, it could not be made to work at a large aperture. Realizing the greater freedom which the substitution of air spaces for cemented surfaces would allow, Rudolph calculated an objective of the type shown in Fig. 104 which was introduced by Carl Zeiss in 1899 as the *Unar*. The Unar had a relative aperture of *f*/4.5. The Tessar may be regarded as a combination of the front half of the Unar and the rear half of the older Protar. The front half consists of a collecting, or positive, lens and a dispersing or negative, lens separated by an air space having a negative effect. The rear half consists of a cemented negative and positive lens, the

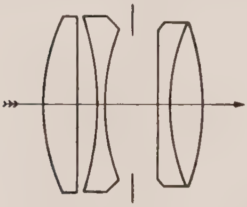


Fig. 102.

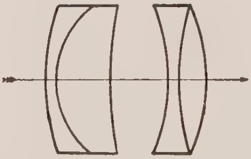


Fig. 103.

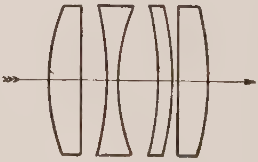


Fig. 104.

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[29] U.S.P. 1,540,752 of 1925.

cemented surface having a collective effect. The front half has a negative focus; the rear is strongly positive. The construction, therefore, is completely unsymmetrical.

This basic design has been one of the most successful yet developed for anastigmat objectives except where a large angular field is necessary or an aperture larger than $f/3.5$.[30]

The following are triplets with cemented rear element and are thus similar to the *Tessar* of Zeiss:

Aldis, Series I and II, $f/4.5$	Aldis Bros.—Birmingham (England)
Tessar, Series Ic, $f/4.5$ Series IIb, $f/6.3$	Bausch & Lomb Optical Co.—Rochester, N. Y.
Saphir, $f/3.5$, $f/4.5$, $f/6.3$	Boyer, Paris (France)
Glyptar, $f/3.5$ and $f/4.5$	E. Busch & Co.—Rathenow (Germany)
Serrac, $f/4.5$	Dallmeyer Ltd.—London (England)
Ektar, $f/3.5$, $f/4.5$, $f/4.7$, $f/6.3$	Eastman Kodak Co.—Rochester, N. Y.
Kodak Anastigmat, $f/4.5$	Eastman Kodak Co.—Rochester, N. Y.
Kodak Anastigmat Special, $f/3.5$, $f/4.5$	
Kodak Process Anastigmat, $f/10$	
Kernon, $f/3.5$ and $f/4.5$	Kern & Co.—Aaran (Switzerland)
Dialytar, $f/2.7$, $f/3.5$, $f/4.5$, $f/6.3$	J. Laack & Soehne—Rathenow (Germany)
Elmar, $f/3.5$, $f/4$, $f/6.3$	E. Leitz—Wetzlar (Germany)
Primotar, $f/4.5$	Hugo Meyer—Goerlitz (Germany)
Anticomar, $f/2.9$, $f/4.5$	Plaubel & Co.—Frankfort (Germany)
Ysar, $f/3.5$, $f/4.5$	G. Rodenstock—Munich (Germany)
Stylor, $f/4.5$, $f/6.3$	Roussel—Paris (France)
Xenar, $f/2.8$, $f/3.5$, $f/4.5$, $f/5.5$	J. Schneider & Co.—Kreuznach (Germany)

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[30] The following is a list of the more important patents for objectives of the *Tessar* type:

Belicke, Bausch & Lomb Optical Co., U.S.P. 1,558,073. Improved correction for coma.

——, Carl Zeiss, B.P. 146,211 of 1917. Recalculation of Tessar to employ more resistant glass types.

Merte, Carl Zeiss, B.P. 146,213 of 1917; U.S.P. 1,479,195. Improved spherical correction.

——, Carl Zeiss, B.P. 273,274 of 1926. Covers angular field of 55° at $f/3.5$.

Lee, Taylor, Taylor and Hobson, B.P. 209,371 of 1923. Apochromatic objective, $f/10$.

Tronnier, Schneider, U.S.P. 1,924,527 of 1933. Simplified design for greater tolerances in manufacture.

Tronnier, Schneider, U.S.P. 2,084,714 of 1937. Improved correction of zonal aberration for an aperture of $f/3.5$.

Warmisham, Taylor, Taylor and Hobson, B.P. 209,371; B.P. 240,508. Constructions employing aspherical surfaces.

Skopar, *f*/3.5, *f*/4.5	Voightlander & Soehne—Brunswick (Germany)
Velostigmat, *f*/4.5	Wollensak Optical Co.—Rochester, N. Y.
Apo-Tessar, *f*/9	Carl Zeiss—Jena (Germany)
Tessar, *f*/2.7, *f*/2.8, *f*/3.5, *f*/4.5, *f*/6.3, *f*/8.0	Carl Zeiss—Jena (Germany)
Novar, *f*/4.5	Zeiss-Ikon—Dresden (Germany)

Development of the Triplet with Cemented Rear Doublet.—In Fig. 105 are shown a number of objectives developed from the triplet with a cemented rear doublet in which the rear half has been made into a cemented triplet. The particular design in (*a*) was issued commercially by Ross Ltd. (London) from calculations by Hasselkus[31] as the *Xpres* in three series—*f*/4.5, *f*/3.5 and *f*/2.7—the last intended more particularly for motion picture work and including a smaller angle than the others. The construction shown in (*b*) was introduced by the Gundlach Optical Company (Rochester, N. Y.) as the *Radiar* with an aperture of *f*/4.5. The third design shown was patented by Carl Zeiss.[32]

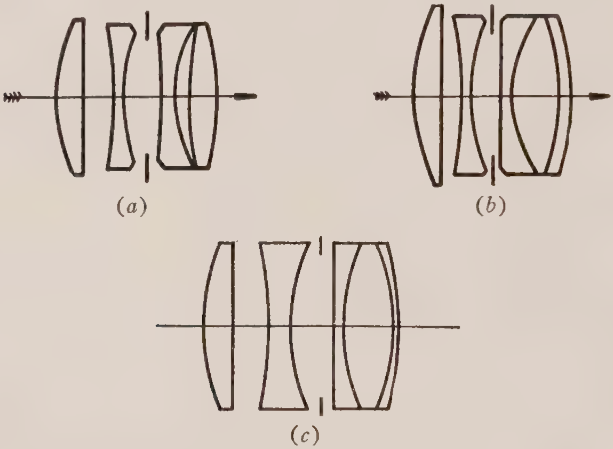

Fig. 105. Objectives Developed from the Triplet with Rear Cemented Doublet.

In each case the three glass design was adopted because it allows a different selection of glasses and affords greater latitude in balancing the opposing powers of component parts of the system to obtain good correction.

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[31] B.P. 29,637 of 1913.

[32] B.P. 256,586 of 1925.

Another method of obtaining greater freedom in meeting the conditions necessary for good correction at a larger aperture or for an increased angular field consists in making both the front and rear elements cemented doublets (Fig. 106). An objective of this design has been placed on the market by Dallmeyer Ltd. (London) from calculations by Booth[33] as the *Pentac* with a relative aperture of $f/2.9$.

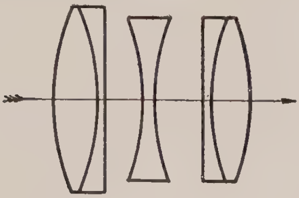

FIG. 106.

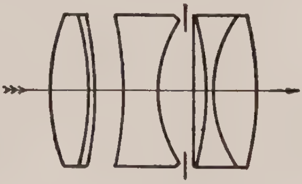

FIG. 107.

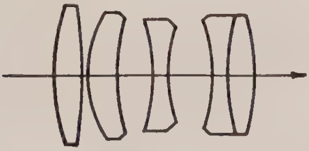

FIG. 108.

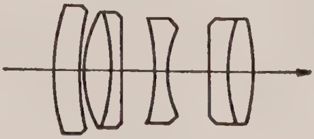

FIG. 109.

In the *Biotessar* $f/2.7$ of Zeiss[34] (Fig. 107) the front element is a cemented doublet and the rear element, a cemented triplet.

Another development of the Tessar design in which the front element is divided into two separated lenses to attain a relative aperture of $f/2.9$ is shown in Fig. 108.[35] Two further designs based upon the same basic principle of subdividing one or more members of the Tessar construction have been patented by Tronnier for the J. Schneider Optische Werke of Kreuznach (Germany). In one of these[36] (Fig. 109) the front converging element is divided into two parts, the second consisting of two cemented lenses. In the other[37] (Fig. 110), the front converging member has likewise

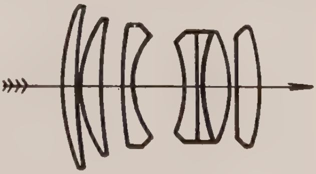

FIG. 110.

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[33] B.P. 151,506.

[34] U.S.P. 1,697,670; B.P. 256,586.

[35] Tronnier, U.S.P. 2,105,799.

[36] Tronnier, U.S.P. 2,076,686.

[37] Tronnier, U.S.P. 2,106,077.

been divided into two single lenses while the rear member consists of a cemented three-glass element followed by a positive meniscus element.[38]

Objectives Developed from the Telescope Objective of Gauss.—The telescope objective of Gauss, in its simplest form, consists of two meniscus lenses separated from each other by an air space and with their concave surfaces facing the incident light. The chief advantage of this construction is the facility which it affords for securing good spherical correction for more than one color. Photographic objectives of this type, therefore, can be designed to produce a higher degree of sphero-achromatism than is possible with other types. This makes the Gaussian design especially favorable for lenses to be used for three-color negative making. Apochromatic Process lenses of this type have been widely employed for many years in three-color photo-engraving and other color reproduction processes.

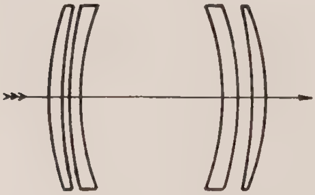

Fig. 111.

The Gaussian design is notable also for the excellent correction obtainable over an exceptionally large, flat field at large apertures. Coma is usually troublesome in symmetrically designed lenses of this type if used at a large aperture; satisfactory correction, however, is possible by departing from a strictly symmetrical construction.

The first photographic objective of this type (Fig. 111) appears to have been designed[39] by Alvan G. Clark of Cambridgeport, Mass., in 1889. It was introduced by the Bausch & Lomb Optical Co. of Rochester (N. Y.) as a portrait lens, but does not seem to have met with much success, as it was soon withdrawn from the market.

The first anastigmatic objective based upon the principle of the Gauss telescopic objective was designed by Paul Rudolph in 1896, and introduced commercially by Carl Zeiss of Jena (Germany) as the *Planar* (Fig. 112).[40]

Rudolph was unable to follow the Gaussian design completely because the glasses necessary for a well corrected objective were not available at the time. In the Planar, the inner lenses are cemented doublets made of glasses having identical refractive index, but different dispersions. Therefore, the inner cemented lenses act as a single lens so far as the refraction of any single color is concerned, while, owing to the difference in the dispersive values of the two glasses, the amount of chromatic aberration may be altered simply by changing the curves of the two cemented surfaces which separate the two mediums of different dispersion. In this way, the chromatic aberration of the two cemented lenses may be made to equalize the chromatic aberration of the two outer lenses so that satisfactory color correction may be obtained at the same time that the astigmatic and spherical errors are corrected. The relative aperture of the Planar is $f/3.5$, but owing to the presence of considerable coma, smaller diaphragms are required for critical definition.

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[38] Other modifications of the basic Tessar design somewhat similar have been patented by Minor (B.P. 187,082) and E. Leitz & Co., B.P. 381,135.

[39] U.S.P. 399,499.

[40] U.S.P. 583,336.

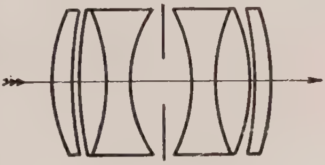

Fig. 112.

Later it was found possible, through choice of suitable glasses and lens shapes, to produce a well corrected objective with only two lenses, thus retaining the essential form of the Gauss design. The problem was solved at very nearly the same time by Kollmorgen who was with Hugo Meyer of Goerlitz (Germany) and by Martin who was associated with the firm of Emil Busch of Rathenow (Germany). Kollmorgen's method was to make each combination of an anomalous glass pair; i.e., the coefficient of refraction of the collecting lens of low dispersion must be as high, or higher, than the dispersing, or negative, lens. The best known objectives of this type are the *Aristostigmat* of Hugo Meyer,[41] the *Omnar* of Busch,[42] the *Homocentric* of Ross Ltd.[43] the *Double Orthar* of Plaubel and the *Process* $f/10$ of Bausch & Lomb, Rochester, N. Y.

A modification of this construction (Fig. 113) has been used for a number of wide angle lenses, among them the Cooke Series VIIb $f/11$ Wide Angle, the Dallmeyer Wide Angle $f/11$ and the Meyer Wide Angle $f/9$. These lenses cover a field of approximately 90° at their maximum aperture. The *Metrogon* (Fig. 114) of Bausch & Lomb has an aperture of $f/6.3$ and an angle of nearly 100°.[44]

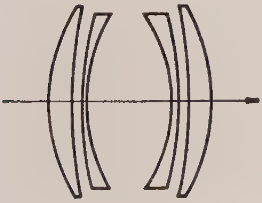

Fig. 113.

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[41] B.P. 20,349 of 1900.

[42] Austrian 8364 of 1901.

[43] B.P. 20,349 of 1900.

[44] U.S.P. 2,031,792.

In general, the aperture of symmetrically constructed objectives of this type does not exceed $f/6.3$ or at the most $f/4.5$. In 1920, Lee of Taylor, Taylor and Hobson Ltd. (Leicester, England) pioneered in the development of large aperture lenses of this construction, and by departing from a symmetrical design, obtained an aperture of $f/2$ for a field of approximately 50° (Fig. 115). This design was placed upon the market as the Cooke *Opic* [45] and has been highly successful. Lee later increased the relative aperture to $f/1.5$, without essentially changing the design, by reducing the size of the field covered to 35°, which is sufficient for motion picture work.[46]

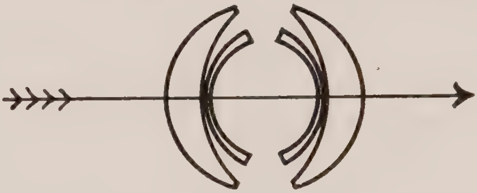

FIG. 114.

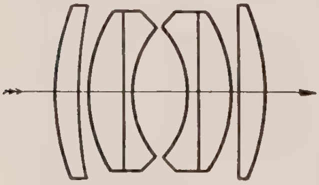

FIG. 115.

A similar design by Merté [47] was introduced by Carl Zeiss of Jena (Germany) as the *Biotar* [47] with a relative aperture of $f/1.4$.

Other lenses of this type are:

Biotar, $f/1.4$	Carl Zeiss—Jena (Germany)
Ektar, $f/1.9$, $f/2.0$	Eastman Kodak Co.—Rochester, N. Y.
Xenon, $f/2.0$	Jos. Schneider—Kreuznach (Germany)

This design, having shown itself to be especially suitable for lenses of large aperture, has found considerable favor with calculators in recent years. One of the most active has been Lee himself, three of whose more recent designs based upon his successful *Opic* are shown in Fig. 116.

In the design shown in (*a*), the aperture was increased to $f/1.5$ by making the inner dispersive components cemented triplets.[48] The aperture was increased to $f/1.4$ for an angle of 40° by dividing the rear collective lens of the earlier *Opic* into two simple lenses as in (*b*).[49] The construction shown in (*c*) is similar to the others, but employs an aspheric surface to obtain an aperture of *f*/1.1.[50] A further development also with aspheric surfaces has a relative aperture of *f*/1.[51] These designs, of course, are intended primarily for motion picture and miniature cameras.

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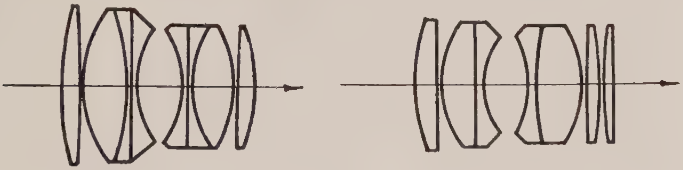
[45] B.P. 157,040 of 1921.

[46] B.P. 377,537 of 1932; U.S.P. 2,117,252 of 1936.

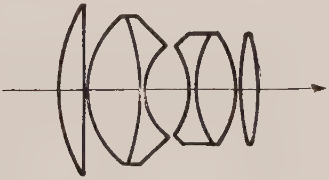
[47] U.S.P. 1,786,916 of 1930.

[48] B.P. 298,769 of 1927.



Lee: *f*/1.5
B.P. 298,769 (1927)
(*a*)

Lee: *f*/1.4
U.S.P. 2,619,895
(*b*)



Lee: *f*/1.1
U.S.P. 2,100,290 (1937)
(*c*)

FIG. 116. Three Large Aperture Objectives Developed by Lee.

In Fig. 117 is shown a design by Paul Rudolph in which the inner dispersing elements are convex rather than concave to the diaphragm, as has been the case with the designs previously mentioned. This construction has been issued commercially by Hugo Meyer of Goerlitz

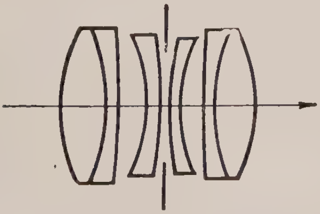


FIG. 117.

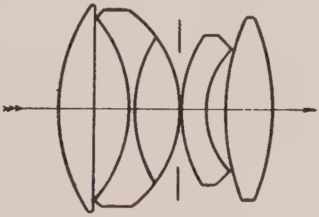


FIG. 118.

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[49] B.P. 373,950 of 1932 and U.S.P. 2,619,895 of 1935.

[50] U.S.P. 2,100,290 of 1937.

[51] U.S.P. 2,100,291 of 1937.

(Germany) as the *Kino-Plasmat* and covers an angle of approximately 30° at $f/2$.[52] A further development of this construction (Fig. 118) patented by Rudolph[53] is for an aperture of $f/1$.

A modification of the Gaussian design (Fig. 119) in which the front converging element consists of two cemented lenses and one of the centrally placed diverging elements is a deeply curved single lens has been patented[54] by E. Leitz of Wetzlar (Germany).

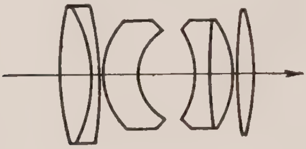

Fig. 119.

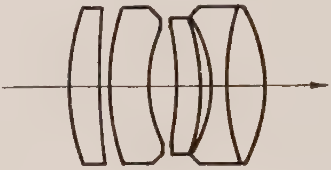

Fig. 120.

A development of the Gauss lens designed by Lee of Taylor, Taylor and Hobson for use in aerial surveying is shown in Fig. 120.[55] This includes an angle of approximately 70°—an objective of 5 inches focal length covers sharply a 7 x 7 inch picture—at a relative aperture of $f/4.5$. Of the four separated components, only one (the second) is dispersive, the rear component being either collective or, in some cases, of zero power. In the usual lens of this type, the order is alternatively collective and dispersive, dispersive and collective. The change results in a larger flat field and improved general correction.[55]

Unofocal.—In 1901, Steinheil introduced as the *Unofocal* an anastigmatically corrected objective (Fig. 121) in which all four lenses are made of glass of practically the same refractive index. Achromatism is secured by a suitable adjustment of the separation between the elements and, while there is neither an abnormal nor normal glass pair, the conditions necessary for spherical and astigmatic correction are satisfied. Spherical correction is obtained by two refractions in the same direction, and astigmatic correction by the two glass-to-air surfaces, which constitute convex and concave surfaces facing a medium of higher refractive index.

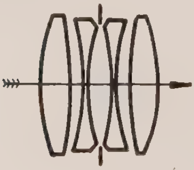

Fig. 121.

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[52] U.S.P. 1,565,205 of 1925.

[53] U.S.P. 1,833,593 of 1931.

[54] B.P. 480,643 of 1938.

[55] B.P. 407,156 of 1934.

The *Unofocal* is made by Steinheil in several series, the most rapid with a relative aperture of $f/4.5$. Among other lenses based upon the same construction are the *Gundlach Anastigmat* $f/6.3$, the Kodak Anastigmat $f/7.7$ and the Graf *Super Anastigmat.* Some of these are symmetrical.

Two other unsymmetrical objectives based upon the same principle may be mentioned, the *Isostigmar* and *Neostigmar* of Beck (London). These, however, are no longer made.

Teleobjectives.—There are two kinds of teleobjectives, one composed of a positive combination, constituting a separately corrected objective, and a negative combination corrected for spherical and chromatic aberration (compound teleobjective), and the other a positive and negative combination which are not individually corrected, the aberrations of the positive component being brought to a minimum by making those of the negative component of the opposite character and as nearly equal as possible (fixed magnification teleobjective).

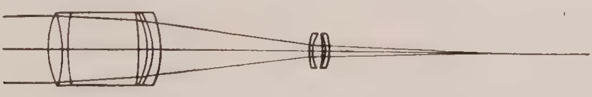

FIG. 122. Compound Teleobjective as Introduced by Dallmeyer Employing a Petzval-type Portrait Lens as the Front Positive Element and a Compound Diverging Element in the Rear.

It is difficult to obtain a large working aperture with the compound teleobjective so, despite the advantage of variable magnification, this type of objective has practically disappeared from the market. Most manufacturers, however, will construct telephoto attachments to order for such of their objectives as may be suitable. The fixed magnification teleobjective has the advantage of producing, with approximately the same camera extension, an image from two to three times as large as the usual camera lens (the magnification varies in different lenses) and its large relative aperture ($f/5.5$ or larger) enables it to be used for rapidly moving objects, sporting events, etc.

The first of the modern fixed magnification teleobjectives was calculated by Martin and introduced by Emil Busch of Rathenow

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BECK—A New Principle in Photographic Lens Construction. Phot. J. **44** (1904) 172.

LEE—Principles and Construction of the Telephotographic Lens. Phot. J. **65** (1925) 392.

(Germany) in 1905 as the *Bis-Telar*.[56] This teleobjective had a relative aperture of *f*/9 and a magnification of 1.65. Teleobjectives of similar design but with greatly improved correction and larger relative apertures have been introduced in recent years. Prominent among these are the *Large Adon* and *Dallon of Dallmeyer* (London), the *Telic* of Taylor, Taylor and Hobson, Leicester (England), and the *Radiar* of Gundlach (Fairport, N. Y.). The first mentioned, calculated by Lan-Davis,[57] has a relative aperture of *f*/4.5 while the second, calculated by Booth,[58] is made in several series [58] with relative apertures ranging from *f*/5.6 to *f*/8. The magnification in all cases is approximately two times. The Cooke *Telic*, calculated by Lee, has a relative aperture of *f*/5.5 and a magnification of two times.[59]

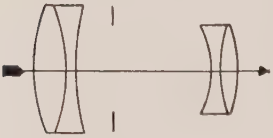

Fig. 123. Fixed Magnification Teleobjective. The *Bis-Telar* of Busch and the *Large-Adon* of Dallmeyer.

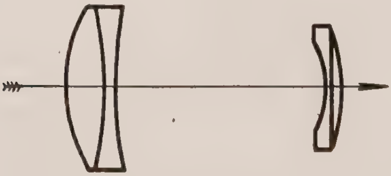

Fig. 124. The *Telic* (2 ×) of Taylor, Taylor & Hobson.

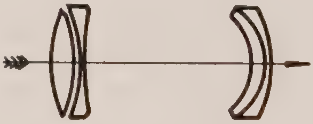

Fig. 125. The *Tele-Tessar* of Carl Zeiss.

The *Tele-Tessar* of Zeiss [60] and the *Telegor* of Goerz differ from the teleobjectives described in the form given the rear component which consists of a pair of cemented meniscus lenses, the positive member being placed nearest the diaphragm and not on the outside. These objectives have a relative aperture of *f*/5.5 and a magnification of two times.

The *Teleros* of Ross Limited (London) is made in two series: one having a relative aperture of *f*/5.5 and a magnification of two times, the other a relative aperture of *f*/6.3 and a magnification of three times. In both cases, the rear component is a cemented triplet (Fig. 126).

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[56] B.P. 15,372.

[57] B.P. 1185 of 1914.

[58] B.P. 139,719 and 151,507 of 1920

[59] B.P. 198,958.

[60] B.P. 179,529, U.S.P. 1,467,804.

A similar objective in which the rear component is a cemented triplet, is made by Taylor, Taylor and Hobson of Leicester (England). This was calculated by Lee[61] and has an aperture of *f*/5.5 and a magnification of three times. The distortion of ordinary telephoto systems was eliminated by Lee (Fig. 128) in a design patented by Taylor, Taylor and Hobson.[62]

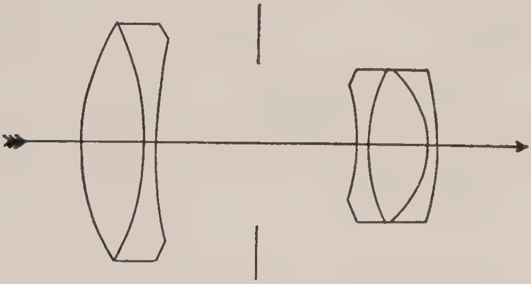

FIG. 126. The *Teleros* of Ross Limited.

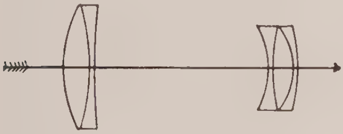

FIG. 127. Cooke *Telic* (3 ×).

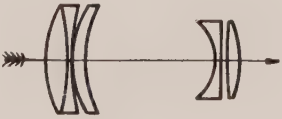

FIG. 128. Non-Distorting Fixed Magnification Teleobjective Patented by Lee.

Types of Lenses Used for Portrait Work.—Four types of lenses are in general use for portrait work:

1. Lenses of the Petzval construction.
2. The anastigmat.
3. The diffused-focus lens.
4. Non-anastigmatic triplet constructions.

The portrait lens of Petzval and its modifications, owing to its curved field, is used today chiefly for head and shoulder portraits. For this purpose it is, however, favored by many portrait workers because of the plastic quality of the image.

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[61] B.P. 132,067.

[62] B.P. 222,709,1924.

Anastigmats working at a relative aperture of *f*/4.5, or larger, are used quite extensively for portrait work particularly for groups and for full and three-quarter figures. The critical definition of lenses of this type is not required in portrait work and in head and shoulder portraits especially may be objectionable since most sitters, unlike Cromwell, do not want every wart and pimple to show. A number of manufacturers therefore provide lenses of the focal lengths commonly employed for portrait work with a means of softening the definition by introducing a certain amount of spherical aberration through alteration of the position of one of the elements of the lens. The biting definition of lenses not provided with such an adjustment may be softened by using diffusion disks over the lens or by covering it with one or more thicknesses of black chiffon. Cutting a small opening in the cloth will make the definition somewhat sharper than when the entire lens is covered.

The diffused-focus lens is preferred by many portrait photographers because it subdues detail, accentuates the feeling of atmosphere about the subject, and the negatives require less retouching. The degree of diffusion is usually controlled by the size of the diaphragm. Diffused-focus lenses require more than ordinary care in focusing and in the lighting of the subject if objectional halos are to be avoided.

For head and shoulder portraits particularly, a lens of relatively long focal length is desirable. A good rule to follow is this: Use a lens whose equivalent focal length is at least twice as great as the diagonal of the photograph. For full-length figures and groups, a lens of shorter focal length may be used as the subject-to-camera distance is greater. A lens having a focal length from 50 to 60% greater than the diagonal of the photograph may be regarded as the minimum.

An important factor in the choice of the focal length of the lens is the size of the studio. To determine the length of the studio required for a lens of any given focal length, regard the average head as being 9 inches in height and the standing figure as 8 feet. Calculate the degree of reduction for the size of image desired and multiply the degree of reduction by the focal length of the lens and add one focal length. The result is the lens to subject distance. It is usual to add 5 feet to this distance to allow for the camera and background. For example, if the focal length of the lens is 20 inches and it is desired to make a head 2 inches high, the degree of reduction is 1/4.5 and the lens subject distance is 110 inches (4.5 times 20 plus 20 equal 110).

Adding to this 60 inches (5 feet) we have a total of 170 inches or 14 feet 2 inches which is the working space necessary.

Wide Angle Lenses.—A number of anastigmat lenses of symmetrical construction, particularly those of the cemented type, when stopped down will cover a larger plate than that for which they are intended and so may be used as a wide angle lens where neither speed nor an extremely wide angle is required. Some medium speed lenses of unsymmetrical construction will also cover a larger plate when stopped down, but, generally speaking, the increase in the size of the field upon stopping down is much less than with lenses of symmetrical construction, so that, with a very few exceptions, lenses of this type will not serve as wide angle lenses when stopped down.

Wide angle lenses, properly speaking, may be divided broadly into two types, namely *medium* and *extreme* wide angle. Lenses of the first class are usually designed to work at a larger aperture and are, for the most part, based upon the Gaussian construction. (See Page 113.) This construction is especially favorable towards a large field at a relatively large aperture. Lenses of this type may have an aperture as large as $f/9.5$, and cover an angle of 90 degrees.

Most extreme wide-angle anastigmatic lenses are unsymmetrical constructions consisting of two cemented lenses on either side of the diaphragm (Fig. 129). This type of lens can be made to cover sharply a very wide angle but cannot be made to work at a large aperture, its usual working aperture being from $f/16$ to $f/18$. As there are no air spaces, and only four reflecting surfaces, it is largely free from internal reflections and is well adapted for use with subjects containing naked lights, such as street lights, electric signs, chandeliers, etc. The *Zeiss Protar* Series V, $f/18$, the Bausch & Lomb *Extreme Wide Angle Protar* and many others are of this type.

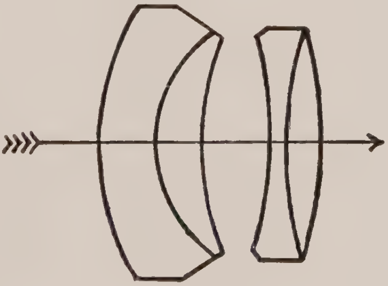

FIG. 129.

Three special purpose wide angle lenses are shown in Fig. 130. The objective shown in (*a*), consisting of two thin hemispherical lenses, was designed by Emil von Hoegh and introduced by Goerz of Berlin as the *Hypergon*. It covers an angle of approximately 135° but as it is not corrected for either chromatic or spherical aberration, the relative aperture is only *f*/40.

The objective shown in (*b*) was devised by Robert Hill[63] for photographing the entire sky at one exposure, and includes an angle of 180°. It consists of a large front lens which contracts the incident angle of the light from the sky to about 90° before it reaches the photographic lens placed on the opposite side of the diaphragm. Good definition is obtained at a relative aperture of *f*/22, but as the chromatic correction is not complete for the whole field, a color filter is advisable.

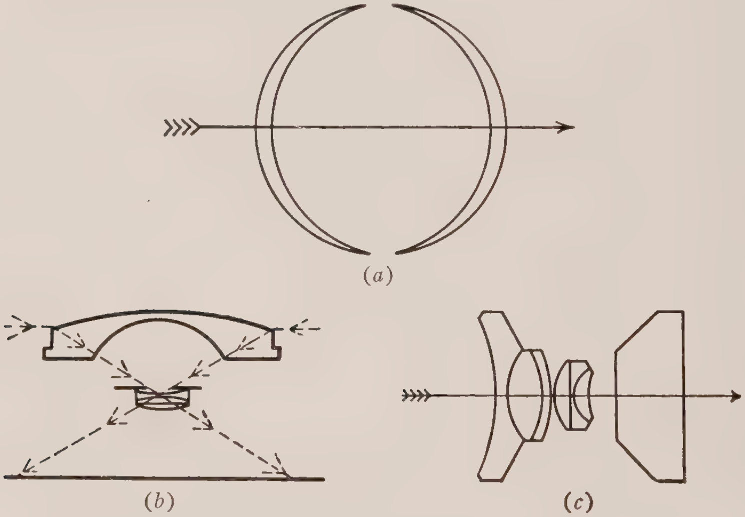

Fig. 130. Extreme Wide-Angle Lenses.

In (*c*) is shown a similar design by Merté of Carl Zeiss with greatly improved corrections and a relative aperture of *f*/8.[64]

Lenses for Aerial Photography.—Lenses designed for aerial photography must have critical definition over a large flat field, must be free from distortion, the illumination of the image must be as nearly uniform, and the relative aperture as large as possible. A relatively wide angle is desirable, if obtainable without the sacrifice of the foregoing essentials. Objectives specially designed and constructed for aerial photography are employed for all mapping and survey work in which the utmost precision is necessary.

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[63] B.P. 225,398 of 1923.

[64] U.S.P. 2,126,126 of 1938.

The *Aviation* lens of the Eastman Kodak Company is of the Tessar type, also the *Aero-Tessar* of Bausch and Lomb, but in this the rear element consists of three cemented lenses as in the Gundlach *Radiar* (Page 110). The *Aero-Xenar* $f/4.5$ of Joseph Schneider is similar to the Pentac of Dallmeyer (Page 111). The *Aviar* lens of Taylor, Taylor and Hobson, the *Wide Angle Xpres* of Ross Ltd. and the *Orthometar* of Zeiss have been noticed on Pages 100 and 106, respectively.

Lenses for Reproduction Processes.—The objective used for copying and process work should give critical definition and even illumination over the entire film, should be free from distortion and, for color reproductions, *apochromatic,* i.e., chromatically corrected for three colors instead of two. These conditions can be satisfactorily met in the present state of photographic optics only through the use of objectives having a relatively long focal length in relation to the size of film or plate which they are designed to cover and a comparatively small aperture, $f/10$ or smaller.

Lenses of this type are designed for use at or near unit magnification, and differ in this respect from other photographic objectives which are designed for use with objects at a greater distance from the lens.

Various designs are used for process lenses. The Gaussian design is one of the most widely employed because of the liberty it affords the designer in securing like spherical correction for different colors. The *Process* $f/10$ of Bausch and Lomb, the *Gotar* and *Artar* of the Goerz American Optical Company, the Kodak *Process* $f/8$, the *Homocentric* Process of Ross Ltd. and the *Apo-Planar* of Carl Zeiss are of this type. The *Apo-Tessar* $f/9$ of Zeiss is, as its name indicates, of the Tessar type. The *Orthostigmat Process* $f/9$ of Steinheil is similar to the other orthostigmats of this firm (Page 96).

Process lenses are favored in certain quarters for commercial photography in the studio where still-life subjects demanding critical definition are involved as well as for three-color photography.

CHAPTER IV

CAMERAS AND ACCESSORIES

Elements of the Camera.—The essentials of a camera are four in number: (1) a light-tight enclosure; (2) a means of forming an image either by means of a pinhole or a lens; (3) a holder for the sensitive material and (4) a means of controlling the time during which light is allowed to reach the film or plate (shutter).

The simplest box camera, in addition to these essentials, is provided with a *finder* to show what will be included in the picture, a *diaphragm* to regulate the amount of light entering the the lens, and a means of changing the film or plate between exposures. Other types of cameras may have a *collapsible bellows,* or a metal tube operated either by a sliding or helical motion, and a *focusing scale* or *screen* in order that the position of the lens may be altered so as to secure a sharp image of objects at different distances from the camera. It may have in addition a *range finder* to measure the distance of the object, *negative carriers* for different types of sensitive material, a *level, depth of focus scale,* built-in *exposure meter,* and various movements to the front and back which alter the position of the lens or the sensitive material in relation to one another.

The Pinhole Camera.—While sharp pictures cannot be made with a pinhole, the image has a pleasing softness which is appropriate for many subjects. In addition, the image formed by a pinhole is always in focus, thus there is no depth of field problem. Furthermore, a single pinhole is equivalent to a battery of lenses, as any desired focal length is obtained by simply placing the pinhole at the corresponding distance from the film.

A simple box camera using a pinhole is shown in Fig. 131.[1] It is designed for use with 3¼ × 4¼ sheet film and is made of cardboard, the edges being sealed with gummed tape. A small opening is cut in the front and over this is placed a piece of black opaque paper. The pinhole is made in this paper using a No. 10 needle, care being taken to obtain a clean-cut, circular opening. A cardboard flap held in place by a metal staple serves as a shutter. An inner retaining ring, formed of cardboard strips glued to the sides of the camera, holds the sheet of film in place against the back of the camera. The lines seen on the side and top serve as a finder—sighting along these lines indicates what will be included in the picture. The camera must be loaded in a darkroom and but one picture may be made at a time. Exposures vary from a few seconds to a minute using a medium speed film. Naturally, the camera must be placed on a tripod or other firm support for the exposure. A picture made with this camera is shown in Fig. 132.

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[1] For full constructional details see Neblette, Brehm and Priest, *Elementary Photography,* Macmillan (New York, 1941).

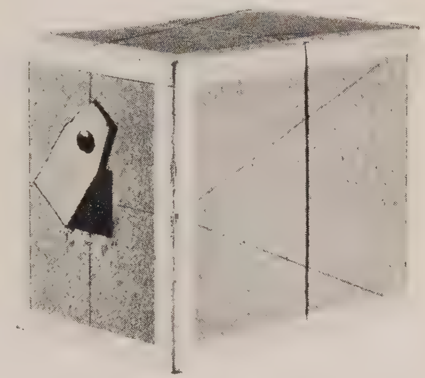


Fig. 131. Simple Pinhole Box Camera.

Box Camera.—The inexpensive box camera is used chiefly by beginners or by those who are interested in photography only to the extent of making record pictures with the least expenditure of thought and energy. The box camera of today is usually designed for roll film as film pack and plate models have practically disappeared in this country. American cameras of this type are usually fitted with single

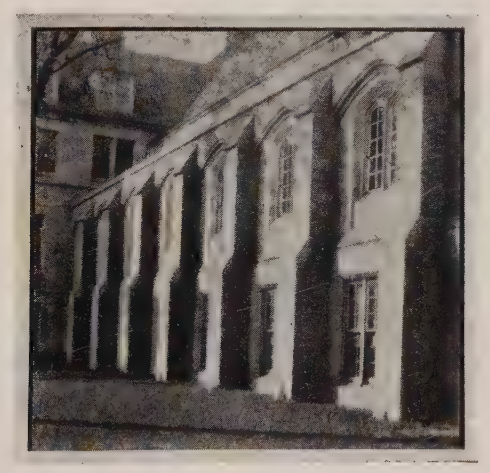


Fig. 132. Picture Made with the Camera Shown in Fig. 131.

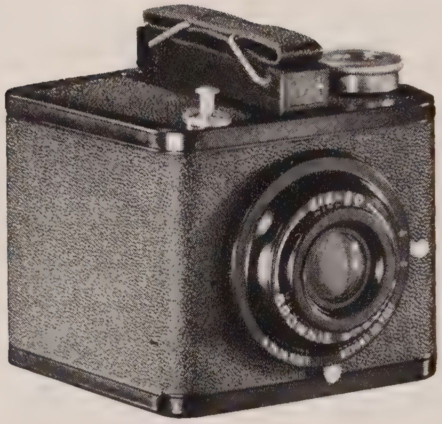


FIG. 133. Typical Box Camera. (Eastman Kodak Company.)

lenses having a maximum relative aperture of about $f/14$ and a simple spring-actuated shutter with one instantaneous speed of about 1/25 second in addition to time and bulb. Even these last are omitted on some cameras. Ordinarily no provision is made for focusing, the position of the lens being fixed so that objects more than 6 to 10 feet, depending on the size of the camera, will be sharp. In recent years, however, cameras with two lenses, one removable, have been introduced. Both lenses together are used for nearby objects and the rear lens alone for distant subjects. In a more expensive form of the box camera, the lens mount revolves, thus changing the separation of the two elements and providing for focusing for three marked positions, near, medium, distant.

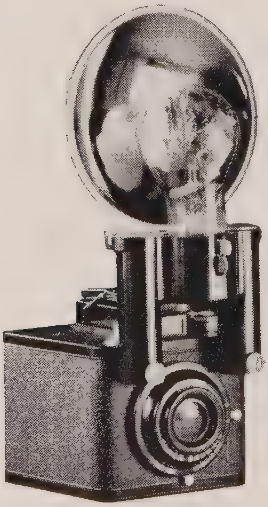
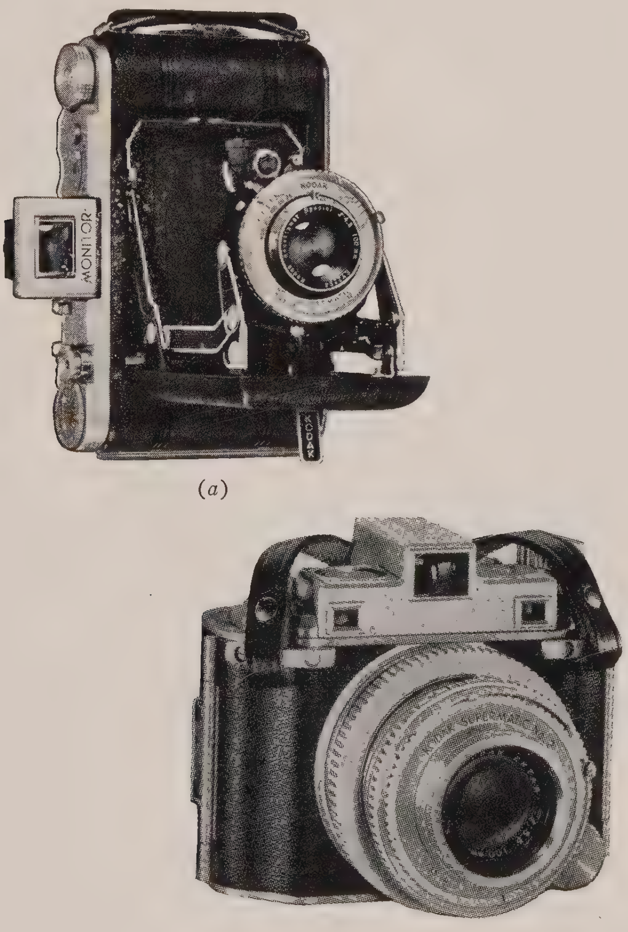


FIG. 134. Box Camera with Synchronizer for Flash Lamps. (Eastman Kodak Company.)

Both framing and reflecting finders (see Page 154) are found on box cameras. A recent trend has been the introduction of models with reflecting finders of approximately the same size as the picture. Another recent development has been the introduction of models with a built-in flash lamp reflector and synchronizer, thus making snapshots possible in dull light outdoors or indoors or at night, thus vastly extending the scope of relatively inexpensive cameras of this type (Fig. 134).

Roll Film Cameras.—The folding hand camera, making pictures from 1 × 1½ to 2½ × 4¼ inches, is one of the most popular types among amateurs and, accordingly, has received particular attention from the manufacturers who have made available many models ranging from the inexpensive camera with single lenses and simple



(*a*)

(*b*)

Fig. 135. (*a*) A Typical Folding Roll Film Camera (Kodak *Monitor*), and (*b*) Roll Film Camera with Coupled Range Finder (Kodak *Medalist*).

shutters to those with anastigmat lenses of large aperture and between-the-lens shutters of high precision. In recent years, designs with a self-erecting front (Fig. 135) have largely superseded the older designs in which the front had to be pulled out by hand. The manufacturers have displayed considerable ingenuity in the designing of a self-erecting front, the principal concern being to produce a smooth functioning movement with a high degree of rigidity when the bellows is fully extended and the front is in position for an exposure. No provision is made for focusing on some of the less expensive models; on focusing models, focusing is accomplished either by partially unscrewing the front element of the lens or by moving the lens and shutter forward or backward on a short track or by means of a helical mount forming a part of the camera front. Metal frame or reflecting finders are usually fitted to the lower-price models; optical-type finders to the more expensive (see Page 154). Range finders are also available on cameras of this type and the number with coupled range finders is growing.

In cameras fitted with reflecting finders, the diaphragm, focusing and shutter speed scales are sometimes placed on the top of the shutter, so that they will be visible with camera held in the hand at waist-level for the exposure.

In most cases, the film is positioned for successive exposures by means of numbers printed on the protecting paper which are viewed through a window in the rear of the camera. Recently, however, several models have been introduced in which the film-transport mechanism positions the film for successive exposures automatically without the necessity of referring to the numbers on the film roll. Usually, in such cases, the film positioning mechanism is connected mechanically to the shutter so as to prevent a second exposure until an unexposed section of the film is in position, thus preventing double exposures.

Hand Cameras Using Cut Film, Plates or Film Packs.—Hand cameras of this type appeal chiefly to the serious amateur as they are more suitable for difficult work than the more convenient roll film cameras. The ability to focus on the ground glass is of great importance in many phases of photography; furthermore, the possibility of using one of the many varieties of cut film, plates, or film pack appeals to the advanced amateur, since it enables him to select the sensitive material best suited to each particular subject. Usually, cameras of this type are fitted with a double extension bellows which enables them to be used for copying and in photographing small objects. A rising and also a sliding front movement are usually provided as well as a wire frame or direct vision finder.

In the smaller, more compact cameras of this type, the focusing screen forms a panel which is interchangeable with the cut film holder or film pack adapter. Invariably, single metal holders are employed. A pressure plate behind the hinged metal frame enables either cut film or glass plates to be used interchangeably in the same holder.

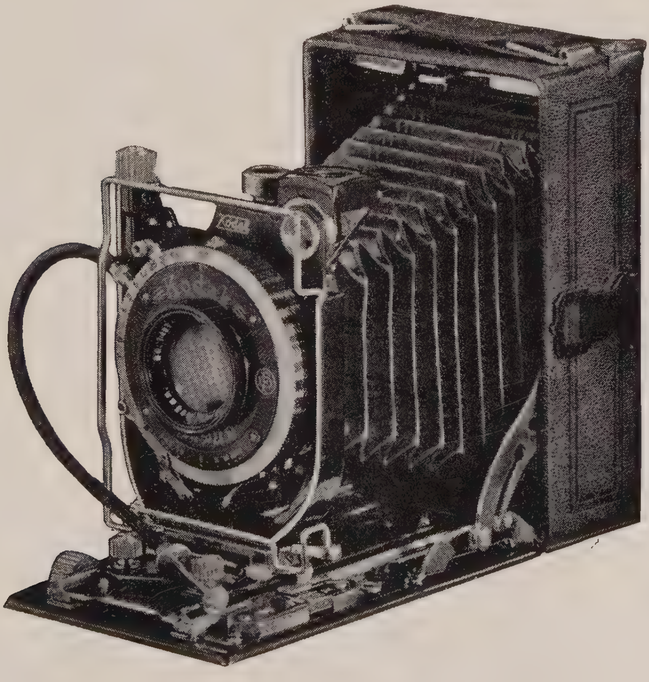


Fig. 136. Cut Film, Film Pack and Plate Camera with Ground Glass Focussing Back. (*Recomar,* Eastman Kodak Co.)

Film and plate cameras of the type shown in Fig. 136 are now almost exclusively of European origin, as American manufacturers have shown little interest in such models in recent years.

Several manufacturers have introduced cameras of this type, generally in sizes from 9 × 12 to 10 × 15 cm., which although adapted to use in the hand, are designed primarily for use on a tripod and are equipped with all of the movements common to the professional camera, including: reversing and swing back, front and side swing, wide angle beds, etc. Such cameras are well suited to the requirements of the serious worker who prefers a smaller size, or greater compactness, than is provided by the professional view or commercial camera.

The Miniature Camera.—The last few years have witnessed a truly remarkable development of the small or *miniature* camera. The term miniature is loosely employed in present-day photographic literature, but for the purposes of this discussion, it will be assumed to mean a camera making pictures $4\frac{1}{2} \times 6$ cm. ($1\frac{5}{8} \times 2\frac{1}{2}$ inches) or smaller.

The miniature camera owes its widespread popularity to the fact that (1) it is light and compact, easily carried and convenient in use, (2) the picture size being small and the focal length of the lens short, the depth of field is such that lenses of much larger relative aperture may be used than are feasible on larger cameras. Thus, lenses with a relative aperture of $f/2$ or larger are fairly common on miniature cameras, whereas lenses with a relative aperture greater than $f/3.5$ are seldom useful on the larger cameras, owing to the limited depth of field. The large aperture lens enables pictures to be made in the home with ordinary lighting, street scenes at night, sporting events indoors, theatre photography by stage lighting and many other phases of photography which would be exceedingly difficult if not impossible with other types of apparatus. Being small and unobtrusive, the miniature camera is well suited

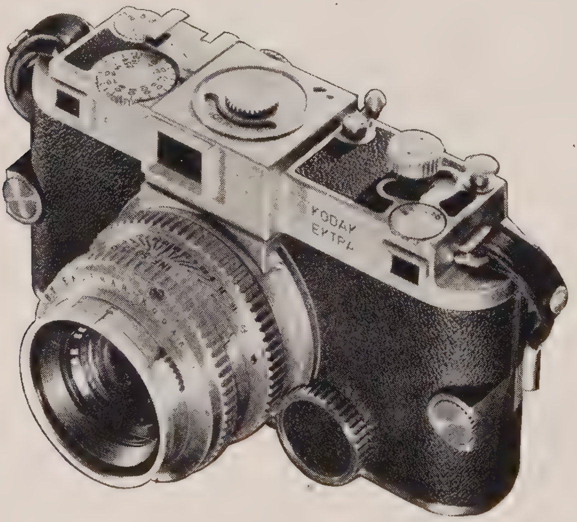


FIG. 137. Typical Precision Miniature Camera. (The Kodak *Ektra.*)

to making pictures without attracting the attention of the subject: the so-called "candid photography."

Another very important factor in the popularity of the miniature camera is the vast amount of ingenuity which has been shown by the manufacturers in the design of instruments of this type and the skilled workmanship displayed in the better examples. The modern miniature camera is a precision instrument which despite its size is capable of producing results in most cases equal to and under many conditions superior to those of larger cameras.

Both scale focusing, twin-lens and reflex cameras are found in this class, but the first-mentioned comprise by far the larger number. These may be divided into two classes: (1) those with a collapsible bellows, and (2) those in which the necessary extension is secured by a metal tube with a sliding or helical-screw motion. A typical miniature camera is shown in Fig. 137.

Among the prominent features of cameras of this type are:

1. *Ready interchangeability of lenses.* Miniature cameras employing focal plane shutters are usually designed to permit the use of a number of lenses, thus enabling wide angle, high speed or telephoto lenses to be used as the occasion demands.

2. *Coupled range finder and focusing.* This enables the distance of the subject to be determined accurately and the lens adjusted for this distance in one operation.

3. *Direct optical view finder.* This frequently is designed to produce an enlarged image, and where the camera is designed for use with different lenses, either the area included is indicated in the field or the finder is designed to be adjustable both with respect to the size of the image and the angle included so as to correspond with the different lenses for which the camera is designed.

4. *Focal plane or high speed between-the-lens shutters.* With the former, most cameras have an interlocking device which results in a new section of film being wound into place when the shutter is being set. This automatically prevents double exposure since the exposure cannot be made until an unexposed section of film is in place. The focal plane shutters are designed to work very close to the sensitive material and consequently possess a very high efficiency. The maximum speed varies between 1/500 and 1/1000 of a second. On cameras using between-the-lens shutters, the Compur shutter is almost universal. The maximum speed of the extra-rapid Compur shutter used on many miniature cameras is 1/500 second.

5. *Film transport.* In most cases, the film spools are carried in light-tight metal magazines; the film being wound from the magazine for the exposure and wound back into the magazine when exposed. The magazine is placed in and removed from the camera in daylight. Daylight-loading roll film, with the conventional paper packing, is used only in those cameras making pictures $4\frac{1}{2} \times 6$ cm. ($1\frac{5}{8} \times 2\frac{1}{2}$ inches) or half this size, namely 3×4 or 4×4 cm. In cameras using a perforated 35 mm. film, the winding key operates a sprocket which engages the perforations along the side of the film. An automatic stop locks the winding key when the amount of film required for the next picture is in place, thus preventing overlapping exposures.

6. *Attachments for specialized work.* One of the very important reasons for the present popularity of the miniature camera is due to the attention which the manufacturers of some of the more popular models have given to the designing of attachments for specialized work. In some cases, there are several hundred such attachments designed for such diverse fields as copying, photomicrography, stereoscopy, and macrophotography, aside from special features such as an automatic film rewind for making a number of exposures in rapid succession, synchronizing photoflash bulbs, self-timers, devices for panoramic photography as well as a full line of equipment for processing miniature camera negatives and printing both by contact and projection. These have made some models of the miniature camera more nearly a universal camera than any other now available.

The Reflex Camera.—The reflex camera is so called from its construction (Fig. 138). A mirror placed at an angle between the lens and the sensitive film reflects the image to a focusing screen at the top of the camera where it is seen right side up and in full size up to the moment of exposure. When the exposure lever is depressed, the mirror swings up out of the way and covers the focusing screen. Upon reaching this position, it releases the focal plane shutter exposing the film or plate. The exposure is governed by the width of the aperture and the rate at which it moves across the surface of the sensitive material. In some reflex cameras, the mirror returns automatically to its original position as soon as the exposure lever is released; in others, an interlocking device makes it necessary to return the mirror to its original position in front of the film before the shutter can be rewound for a second exposure. This prevents accidental exposure.

Reflex cameras are available in a wide variety of models. The smaller are usually designed for use with roll film; however, in the larger sizes it is usually possible to use cut film or plates, either in holders or a changing box (magazine), film packs in an adapter; or roll film in a detachable roll film holder.

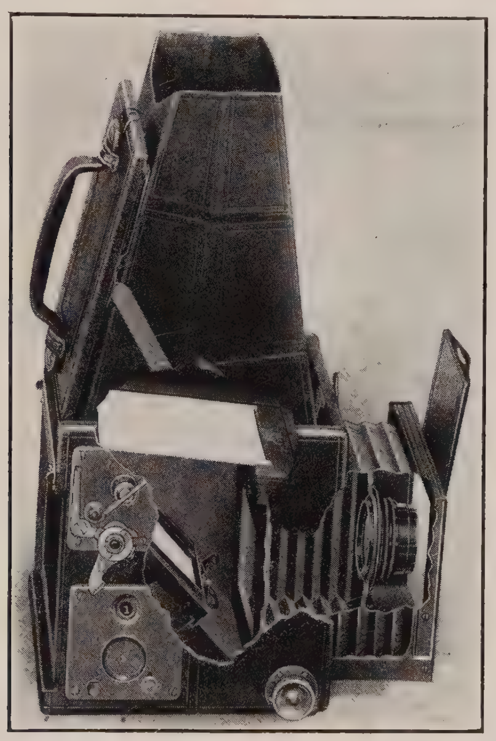


FIG. 138. Principle of the Reflex Camera.

The reflex camera is favored by those who wish to be able to see the image on the focusing screen so as to study the arrangement of the subject to better advantage, but object to the inconvenience of the stand camera. Also it is one of the best types of cameras for photographing rapidly moving objects since the focusing arrangements enable the moving object to be kept properly placed in the picture and in sharp focus while the focal plane shutter makes possible the rapid shutter speeds required to stop motion.

The Twin Lens Camera.—This type of camera (Fig. 139) consists essentially of two cameras with matched lenses, one of which is used for focusing and arranging the subject and the other for making the picture. Cameras of this type are made in sizes 2¼ × 2¼ and smaller; above this size the camera becomes rather bulky. The twin lens camera allows the image to be followed on the focusing screen to and during the exposure. There is no delay in exposure, as in the reflex, where time must be allowed for the swinging mirror. On the other hand, the images on the focusing screen and the film do not coincide exactly because of the separation of the two lenses. This is known as the parallax error and is unimportant in practice except in nearby subjects. Certain cameras of this type are fitted with devices which compensate for the parallax differences by masking the finder image.

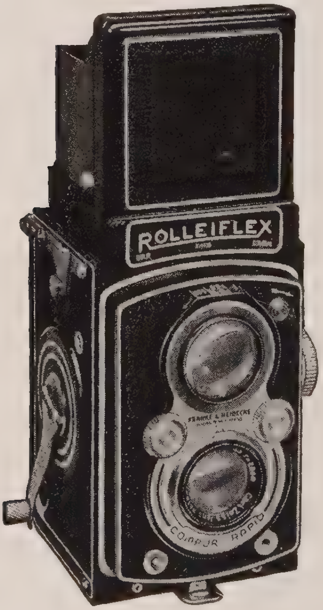


FIG. 139. Twin Lens Camera (Rolleiflex).

The twin lens camera does not offer the same facility as regards interchangeability of lenses as other cameras, since in this case, it is obvious that not one but two lenses are required. In its modern form, however, it is deservedly popular on account of its simplicity, the ability to focus the image as in the reflex camera, and its ruggedness and general dependability.

Professional Cameras.—The so-called *view* camera (Fig. 140) is intended primarily for general exterior and interior photography. It is designed for use with cut films or plates and is made as light and portable as is consistent with strength and rigidity. Usually it has a long bellows extension, may be focused from either the front or the rear, and the movements include a rising front, side and vertical swings to the back, and reversing back. It must be used on a tripod as it does not have either a finder or a focusing scale.

The *commercial* or technical camera (Fig. 141) has a much wider range of movements so as to meet the most exacting demands of technical photography. The vertical and horizontal swings have a much wider range than in the view camera and the front likewise is fitted with similar swings thus simplifying the photographing of tall buildings, cramped interiors, and commercial or industrial products requiring unusual perspective.

The *commercial studio* camera (Fig. 142) is similar except that it is heavier and more substantially constructed, since weight is not as important as in a camera intended for use outside the studio. A rigid stand enables the camera to be raised to a height of from eight to nine feet from the floor and inclined to any desired angle.

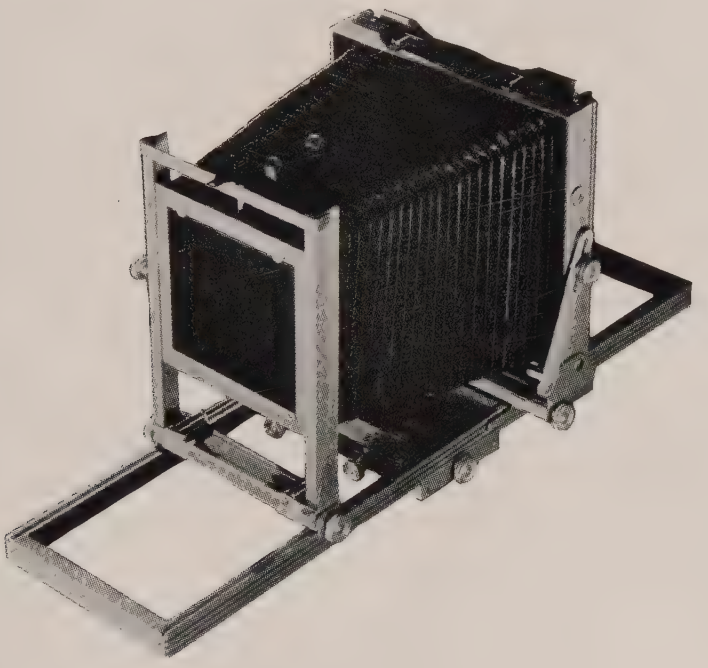


FIG. 140. All-Metal View Camera. (Eastman.)

Cameras designed for professional *studio portraiture* (Fig. 143) have a long bellows and are substantially built, particularly in the front, so as to accommodate the long-focus, large aperture lenses desired in portrait work. Cameras of this type are focused from the rear, and the back is provided with vertical and horizontal movements. A sliding carriage enables two pictures to be made on one film or plate. In some cases, this sliding carriage is so designed that the loaded film or plate holder may be placed in one side and the slide withdrawn before the image is focused. Then when the subject is arranged and the image focused, the shutter is closed and the carriage shifted to place the film or plate in position for the exposure. This greatly reduces the time elapsing between focusing and the exposure and is of real assistance in securing more lifelike portraits.

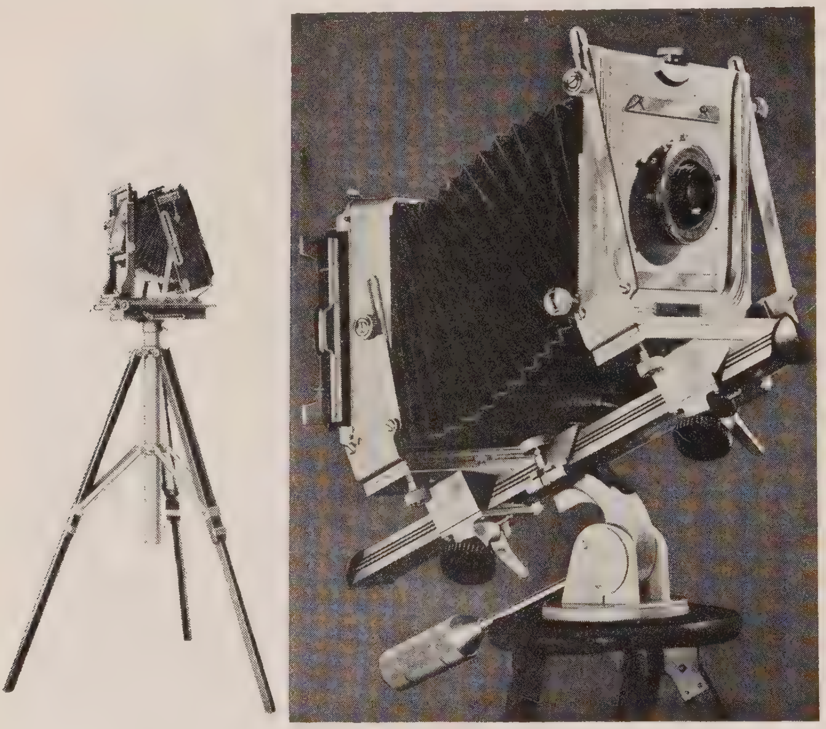
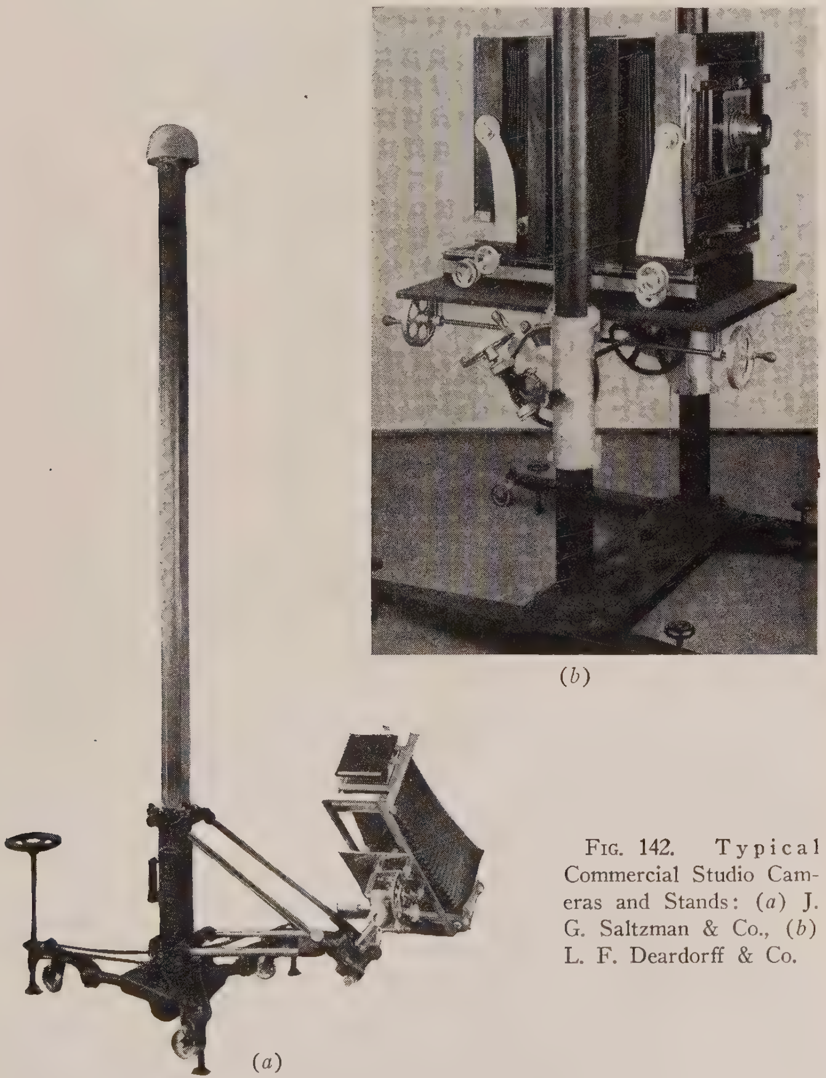

(*a*) (*b*)

Fig. 141. Typical Cameras for Commercial Photography: (*a*) Century Universal, (*b*) Graphic View.

An integral part of the outfit for studio portraiture is a strongly constructed stand which enables the camera to be raised from a position a few inches above the floor to an elevation of about five feet and provides means for inclining the camera at an angle.

Press Cameras.—Cameras of nearly all types are used as occasion demands for press photography, but the camera usually associated with press photography is a rigidly constructed hand camera using cut film, plates, or film pack, and fitted with a focal plane as well as a between-the-lens shutter. Focusing is usually by a scale except when conditions permit the use of the ground glass focusing panel at the rear of the camera. Cameras in which a range-finder is coupled to the lens so that the latter is automatically focused when measuring the distance of the subject are a recent introduction. A wire frame or a direct vision optical finder enables moving objects to be located readily with the camera held at eye level. A synchronizing device for simultaneous


(b)

(a)

Fig. 142. Typical Commercial Studio Cameras and Stands: (*a*) J. G. Saltzman & Co., (*b*) L. F. Deardorff & Co.

operation of the camera shutter and a photoflash lamp is usually fitted and in some models is incorporated in the camera itself.

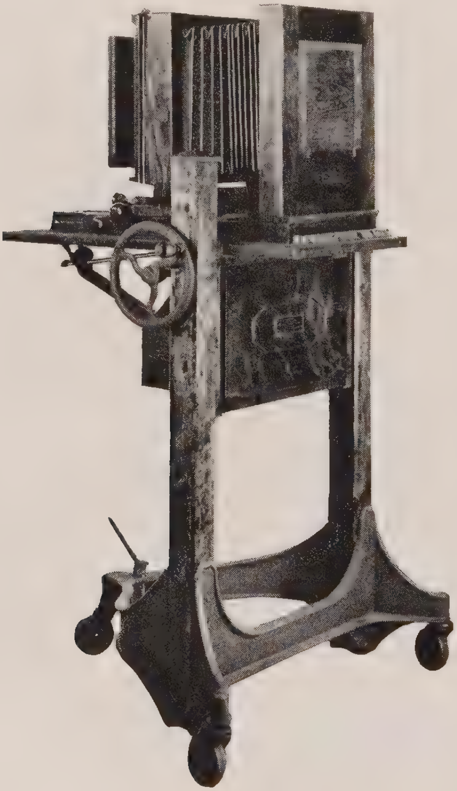


Fig. 143. Century Studio Camera for Professional Portrait Photography. (Folmer Graflex Corporation.)

Special Purpose Cameras.—Fig. 145 shows a camera used for photographing finger prints, signatures, meter dials and the like. In use, the open end of the camera is placed against the surface of the object to be photographed and the exposure made by means of the light supplied by small electric lamps, concealed within the hood, utilizing the current from dry cells contained within the camera. There is no provision for focusing, as the camera is designed to work at a scale of 1 : 1 (i.e. the image is the same size as the object photographed).

A camera outfit designed especially for making identification pictures is shown in Fig. 146. Cameras of this type are designed to be as nearly automatic and as economical in operation as possible. Motion picture film is employed as a negative material in many cases, and frequently no negative is made, the exposure being made on direct positive paper (in rolls) which is reversed in processing to form the completed positive. Since it is important that pictures made for identification purposes should not be transposed from left to right, a reversing prism is used when the photograph is made directly on positive paper.

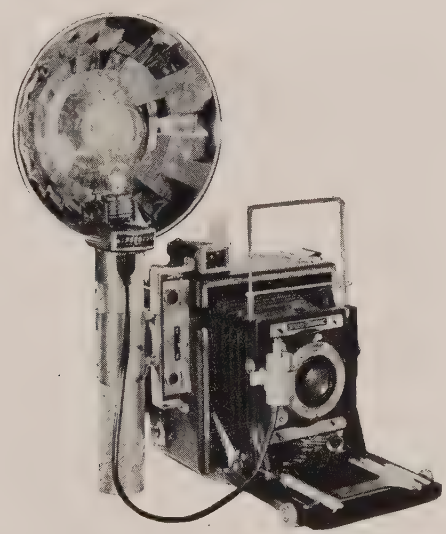


FIG. 144. Speed Graphic Camera for Press Photography. (Folmer Graflex Corporation.)

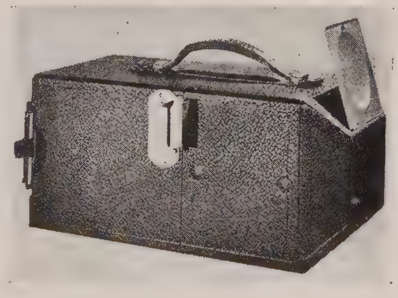


FIG. 145. Fingerprint Camera. (Folmer Graflex Corporation.)

A camera designed especially for making copies of books, magazines, and other printed matter on film for filing purposes is shown in Fig. 147. Micro filming of printed material has grown to considerable importance and there are a number of cameras available together with specially designed enlarging equipment for reading the copied material. In most cases, the cameras are designed to use 35 mm. motion picture film; in others, 16 mm. film is used as in the Recordak which is extensively used by banks to photograph the checks passing through their hands.

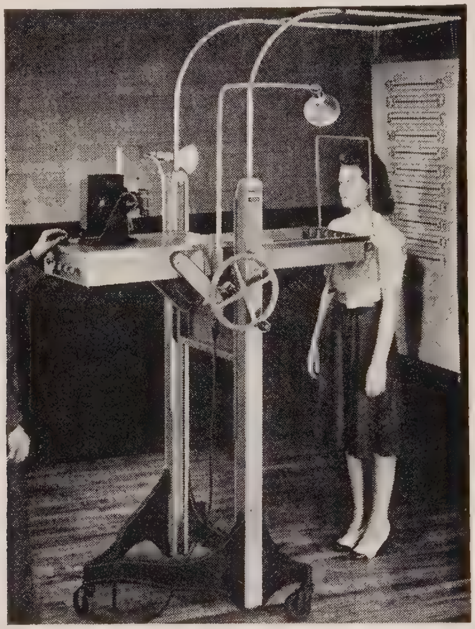


Fig. 146. Photographic Equipment for Making Identification Photographs. (Folmer Graflex Corporation.)

Cameras designed for photoengraving, lithography and other forms of photomechanical reproduction are of two types, one in which the camera back is built into and forms a part of the wall of the processing darkroom, and the other (Fig. 148) in which the sensitive material is placed in a holder which in turn is placed in the camera in daylight as in ordinary photographic practice.

In either case, the camera is large and substantially built on a bed which also supports the easel and is provided with shock absorbers to take up any outside vibration which would affect the sharpness of the image. Arc lamps are usually employed for illuminating the copy, although the use of water-cooled mercury-arc lamps is increasing. The lever shown on the side is for adjusting the distance between the half-tone screen and the sensitive plate. The chains and gears shown on the bed are to enable the operator to change the position of the easel so as to place the copy properly on the sensitive material, to change the size of the image or to focus it sharply without leaving his position at the focusing screen.

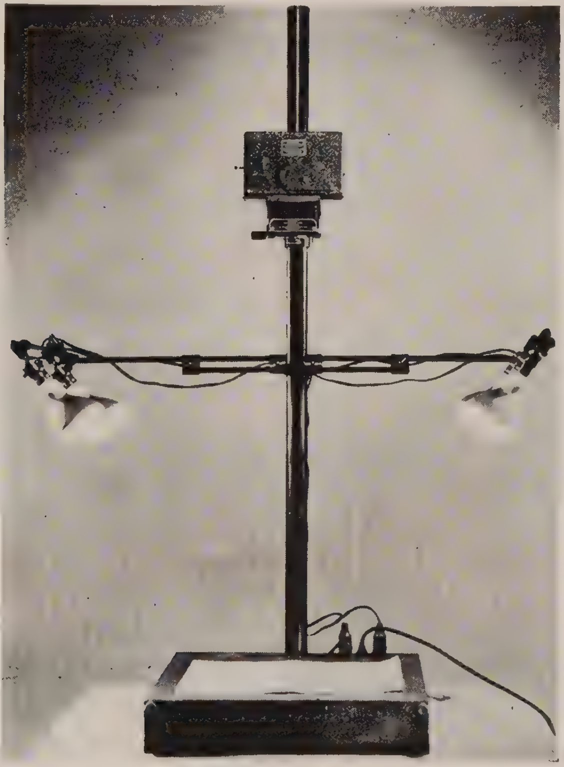


Fig. 147. Camera for Photographing Books, Newspapers and Other Printed Matter on 35 mm. Film. (Folmer Graflex Corporation.)

The term panoramic is applied to revolving cameras designed to make long narrow or panoramic pictures of groups, landscapes and other exterior subjects. Only one camera of this type—the Cirkut[2]—is now on the American market. This camera (Fig. 149) is mounted on a special tripod and a spring driven mechanism revolves the camera during the exposure so that the lens traverses the greater part of a circle. The movement of the image, caused by the moving lens, is overcome by

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[2] Folmer Graflex Corp., Rochester, N. Y.

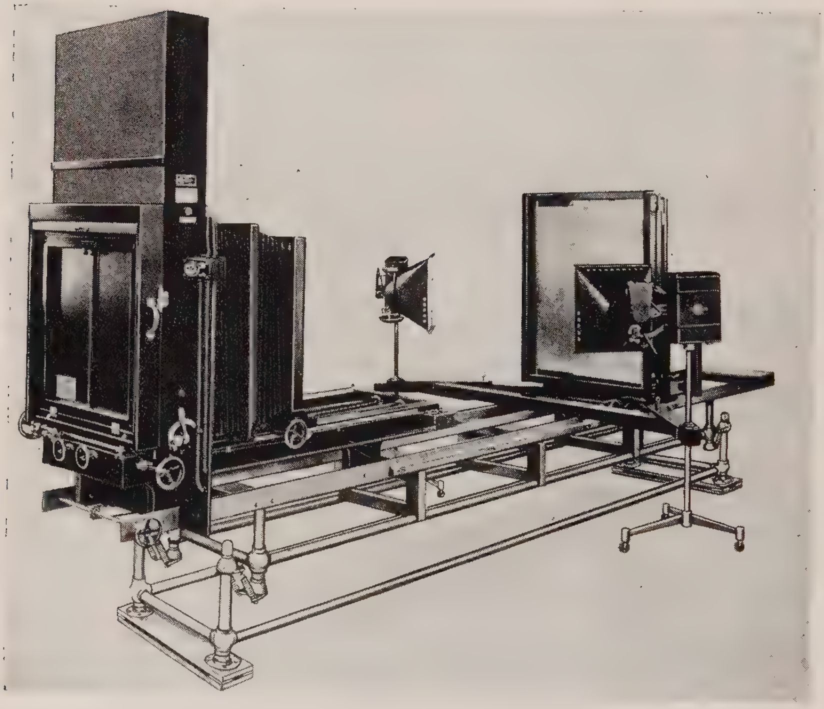

FIG. 148. Camera Used in Photo-Mechanical Reproduction Process Work. (Robertson & Co.)

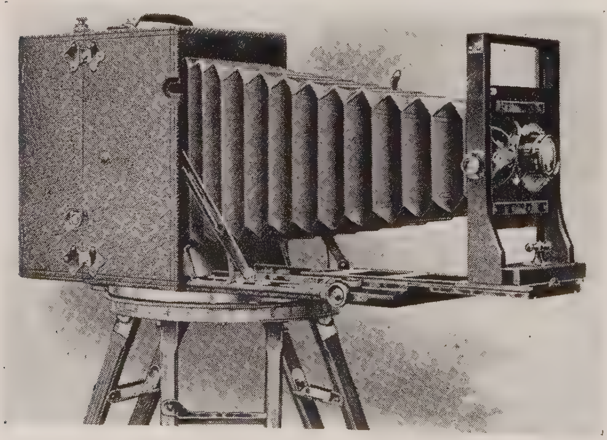

FIG. 149. Panoramic Camera (Cirkut). (Folmer Graflex Corporation.)

moving the film at the same rate by the same driving mechanism, so that a sharp image will be obtained despite the movement of the lens during the exposure.

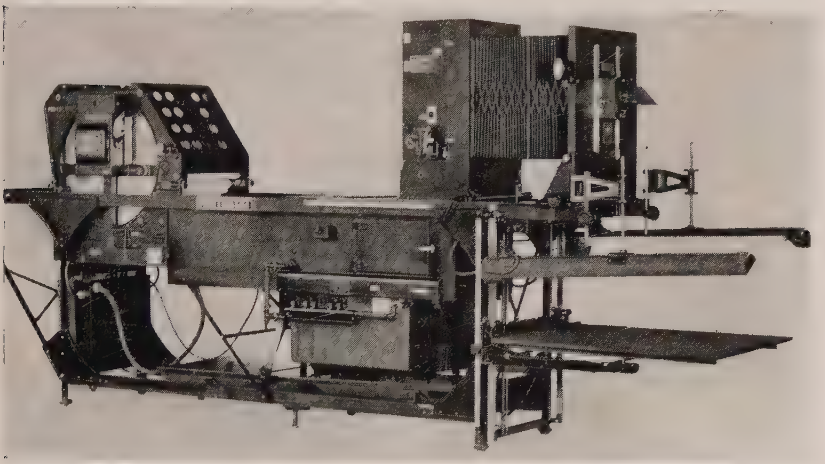

FIG. 150. Camera for Copying Printed Matter Direct on Sensitized Paper (Photostat). (Photostat Corporation.)

In Fig. 150 is shown a camera designed for photographing documents, charts, maps and similar material directly on photosensitive paper.

The Photostat[3] and the Rectigraph[4] are the best known of such cameras on the American market. A prism is used before the lens to reverse the image so the negative copy on the paper will read correctly from left to right. Such photocopies, widely known as "photostats," are exact, require no proof-reading and are acceptable as legal evidence in courts. These machines are designed for operation in daylight and require no darkroom. The special photocopying papers used are supplied in rolls and the exposures are developed, washed and dried as a continuous process in some models.

While stereo-photographs may be made with an ordinary camera by making in succession two pictures separated by a distance equal to that between the eyes (approximately 63 to 69 mm. (2½ inches)), or by means of a stereoscopic attachment (Page 166), the first of these methods is suitable only for still life. There has been little interest in

[3] Photostat Corp., Rochester, N. Y.

[4] Rectigraphic Division, The Haloid Co., Rochester, N. Y.

stereoscopic photography in recent years and all such cameras are now imported, the usual sizes being 45 × 107 mm. (1¾ × 4¾ inches) and 60 × 130 mm. (2⅜ × 5½ inches). The cameras available are of the box type fitted with two matched (identical) lenses and shutters, the latter being interconnected so that both exposures are made at the same time.

The lenses are either mounted solidly on the camera front (fixed focus) or side by side on a movable lens front which enables both to be focused simultaneously. In the example shown,[5] the center lens produces an image on a focusing screen at the top of the camera beneath the hood. Stereoscopic cameras use either roll film, film packs, sheet film or plates. The general practice is to make transparencies on film or glass for use in the stereoscope rather than prints on paper because of the greater brilliance obtainable with images illuminated by transmitted light. In some cases the camera is designed so that it may be also used as a stereoscope.

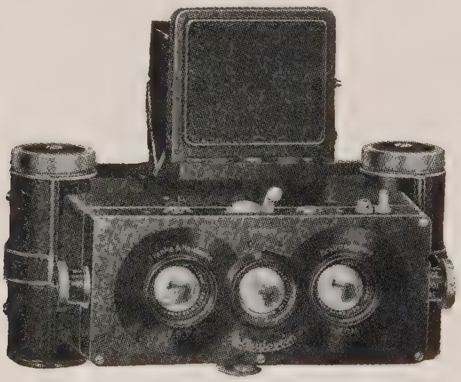

FIG. 151. Camera for Making Stereoscopic Photographs.

CAMERA ADJUSTMENTS

Swing Back.—The swing back is a movement, found quite generally on professional cameras and occasionally on film and plate cameras designed for the serious amateur, which permits the plane of the sensitive material to be placed at an angle to the optical axis of the lens, for the purpose of (1) changing the shape of the image, or (2) securing greater depth of field.

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[5] Burleigh Brooks, Inc., New York.

When the plane of the sensitive material is parallel with that of the subject, parallel lines in the subject are rendered parallel on the image. If, however, the plane of the sensitive material is inclined towards that of the subject, as in Fig. 152, the image is distorted and the lines diverge.

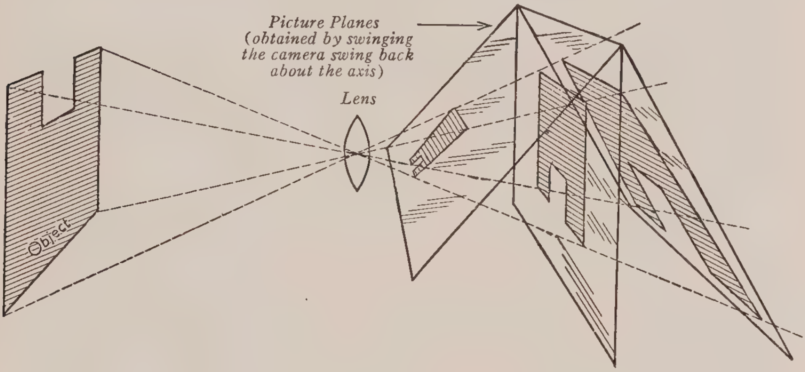

FIG. 152. Illustrating the Effect on the Image of Inclining the Plane of the Sensitive Material to That of the Subject.

Tilting the sensitive material in the other direction causes the lines to diverge but in the opposite direction. Inclining the plane of the subject would produce precisely the same result.

In photographing a tall building, for example, it is frequently necessary to tilt the camera in order to include all of the building. With the sensitive material in its normal plane, that is at right angles to the camera axis, the lines of the building converge towards the top. The swing back, however, enables the sensitive material to be placed in the vertical position, thus securing non-distorted rendering.

In photographing from an elevation, the same principle applies except that the conditions are reversed.

Since the axis of the lens is no longer at right angles to the sensitive material, but crosses it obliquely, a smaller diaphragm is usually necessary to obtain sharp focus over the whole of the image.

Since it is clear from the principles of image formation that the focal distance for near objects is greater than for more distant objects, it is possible under certain conditions to secure sharp focus on both near and distant objects with a relatively large aperture by the simple expedient of inclining the sensitive material. The principle involved is shown diagrammatically in Fig. 153.

A and *B* represent two objects at different distances from the lens and *A′* and *B′* the corresponding image points. It is evident that with the sensitive material at right angles to the optical axis, there is no point at which the image of both *A* and *B* will be sharp, and only by placing the sensitive material between *A′* and *B′* and using a small diaphragm can a sharp image of both be obtained. If, however, the sensitive material is inclined as indicated by the line *A′B′*, both points will be sharply rendered.

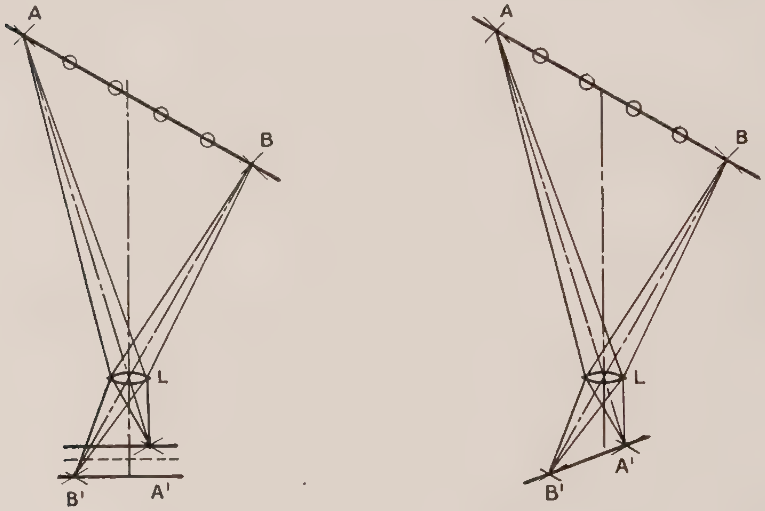

Fig. 153. Placing the Sensitive Material at an Angle to the Optical Axis to Image Sharply Objects at Different Distances.

It is obvious that the swing back may be used in this manner to increase the effective depth of field only if points *A* and *B* lie at some distance above one another. This, however, is frequently the case in practice, as for example, with a group of persons arranged in rows behind one another in a staircase formation, a banquet table, a street photographed from an elevation, etc.

A horizontal swing back may be used in the same way when photographing objects at different distances, on a horizontal rather than a vertical plane. When necessary, both the vertical and horizontal swings may be used in conjunction.

The use of either the vertical or horizontal swings in this manner distorts the drawing of the subject which, in some cases, is objectionable and in other cases desirable. In fact, the commercial photographer frequently uses the rear swings of the camera to regulate the relative size of the near and more distant parts of the image. Thus, with a subject one side of which is appreciably nearer the camera than the other, the horizontal or side swing may be used either to increase or decrease the apparent distance (Fig. 153), while the vertical swing, or swing back, may be used in the same way to regulate the size of objects in the foreground in relation to other objects at a distance.

The Swing Front.—The swing front is an adjustment enabling the lens to be tilted upwards or downwards so as to change the angle of the optical axis with respect to the sensitive material. It is a movement which is found on few cameras except those designed for difficult work of a technical nature.

The swing front may be used in much the same way as the swing back to increase the effective depth of field, but with the advantage that the perspective is not distorted to the same degree. It is useful also in avoiding the necessity for a small diaphragm when the swing back is used to keep the sensitive material vertical. When, for example, the camera is inclined upward to include the top of a tall building, and the swing back is placed in a vertical position, a small diaphragm is often required to render both the top and bottom of the building sharp. If, however, the camera is fitted with a swing front, the use of a small diaphragm may be avoided by inclining the lens so that its optical axis is approximately parallel to the sensitive material.

The use of the swing front in any case is practical only when the lens will cover sharply a picture area larger than that on which it is being used.

Sliding Front.—This movement allows the lens to be moved in a horizontal direction parallel to the film or plate. On hand cameras not fitted with a reversible back, it serves as a rising and falling front, when the camera is placed on its side to make a horizontal picture. On cameras designed for professional use, it is frequently useful in obtaining unusual viewpoints and in distorting perspective to secure striking effects. Like all such movements, it presupposes the use of a lens with greater covering power than the plate or film with which it is used.

Reversible and Revolving Back.—The reversible or revolving back allows the back of the camera to be changed so that the picture may be made either horizontally or vertically without turning the camera on its side. The revolving back, as its name indicates, revolves

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Cook—Swing's the Thing. Phot.Tech. **2** (1940) July p. 42, Aug. p. 35.

from a horizontal to a vertical position without being detached and is found on only a few cameas. Neither reversible nor revolving backs are found on roll film cameras nor on compact hand cameras using plates or sheet film.

SHUTTERS

Modern shutters may be divided into four classes: (1) those placed before the lens, (2) those placed behind the lens, (3) those placed between the lens and (4) those placed near the focal plane directly in front of the sensitive material.

Before-the-Lens Shutters.—Before-the-lens shutters are used on box and other cameras fitted with single lenses. Those used on box, and other inexpensive cameras, consist essentially of a thin metal disk with an open slot which is made to pass in front of the lens by a spring. This type of shutter is adjustable for time, for bulb, and a single "instantaneous" speed which may vary from 1/20 to 1/30 second depending upon the camera.

On larger cameras, the before-the-lens shutter is virtually obsolete except for a single type used by professional photographers. This is similar to the modern between-the-lens shutter except that it has no marked instantaneous speeds and is mounted so as to be readily attached to the front of the lens mount thus permitting it to be used on a number of different lenses.

Behind-the-Lens Shutters.—Behind-the-lens shutters are used chiefly on professional view, commercial or portrait cameras. One type, now nearly obsolete, consists of one, or in some cases two, metal leaves which operate in the same manner as a door. The two leaves are kept in the closed position by means of a spring. The exposure is made by means of a bulb and tubing which compresses the air within a cylinder and operates a piston causing the leaves to swing open and uncover the lens. While this type of shutter is not suitable for extremely short exposures, it can be made almost noiseless in operation which is an advantage in portrait work.

By far the most widely used behind-the-lens shutter consists of two, or in some cases three, metal, hard rubber or plastic blades which are kept overlapping in the closed position by means of a spring. Compression of the air within a cylinder operates a piston which causes the blades of the shutter to make a partial revolution about pivoted points thus uncovering the lens. Upon releasing the pressure on the bulb, the spring tension causes the blades of the shutter to move in the opposite direction thus closing the opening. This type of shutter is more compact than the type previously described and is better adapted to short exposures. With some models, exposures of approximately 1/25 second are possible.

Between-the-Lens Shutters.—Between-the-lens shutters are frequently referred to as diaphragm shutters because of their location near the diaphragm. In some cases, the blades of the shutter are made to serve as a diaphragm opening up only to the set value.

The modern between-the-lens shutters consist of three, or more, thin, hard-rubber, metal or composition blades which are pivoted about fixed points in a circle. These blades are opened and closed by pins on a movable ring. A spring provides the motive power to move this ring through a portion of one revolution. Usually the blades open and close at a fixed speed which is governed by the tension created by the driving spring. The time which the blades remain open is controlled either by pneumatic action or by a series of retarding gears. The former consists essentially of a cylinder and piston, the air being either compressed or partially exhausted in the setting of the shutter. An adjustable leak, which is controlled by the speed setting on the shutter dial, delays the action of the spring on the inner movable ring controlling the shutter blades and thus fixes the time during which the lens is uncovered. In gear-controlled shutters, a chain of gears with an escapement somewhat similar to that on a watch is employed to delay the closing of the shutter blades until the desired time has elapsed.

Focal Plane Shutters.—The focal plane shutter is so termed because it is placed near the focal plane, immediately in front of the sensitive material. Shutters of this type are used on reflex cameras and on many miniature cameras. While reflex cameras have been designed with other types of shutters, the focal plane shutter is particularly suitable since it operates behind the mirror, thus enabling the lens to remain open at all times for observing the image and focusing. (See Reflex Camera.) On miniature cameras it enables different lenses to be used without having a separate shutter for each and in addition the operation of resetting the shutter and the movement of the film may be so connected as to prevent double exposures.

There are two variations of the focal plane shutter: (1) the fixed and (2) the variable slit. The first consists of a relatively long opaque curtain of cloth, or other suitable material, running between a pair of rollers on opposite sides of the picture area, one of the rollers being under tension. The curtain is slightly wider than the picture and the edges are enclosed in grooves which serve the double purpose of forming a guide for the passage of the curtain from one roller to the other and protecting the sensitive material from light. Across this curtain, at distances slightly greater than that between the two rollers are a number of slits of varying widths.

Preparatory to making an exposure, the shutter is set by winding the curtain so as to select a slit of the proper width and the spring tension on the lower roller is adjusted so as to regulate the speed at which the open slit passes in front of the film or plate. These adjustments are made in accordance with a table affixed in a convenient place on the outside of the shutter indicating the width of the slit and tension setting for a given exposure. When the shutter is set, the plate or film is protected by an opaque portion of the curtain. Upon releasing the exposure lever, the curtain is freed and the tension on one of the rollers, usually the lower, causes it to revolve, winding the curtain on it so that the slit passes rapidly in front of the sensitive material thus making the exposure. A locking device stops the curtain after the slit has passed in front of the film or plate thus preventing a second exposure.

The variable slit shutter differs from that just described in having two curtains one directly in front and as close to the other as practical and each has its own pair of rollers. Springs attached to one set of rollers, usually the lower, keep the curtains under tension. Each curtain may be wound up separately but both move downward across the face of the film or plate at the same rate when freed by the exposure lever. The height of the slit in one of the curtains is approximately the same as that of the picture.

Before making an exposure this curtain is wound up on the free roller. The second curtain, however, is only partially wound up. Consequently, it does not completely cover the slit in the first curtain but leaves an open slit the height of which can be varied as required by the extent to which the second curtain is wound up. Thus the width of the opening between the two curtains may be varied at will, so as to control the amount of light reaching the film and thus determine the exposure.

This type of shutter is rather more complicated than the other but has the advantage that a wide range of exposures may be obtained by varying the width of the slit, thus rendering less necessary the dependence upon variations in spring tension as a means of controlling the exposure. Furthermore, a shutter of this type may be graduated to read directly in terms of exposure and is the only type really practical for miniature cameras.

On reflex cameras the mirror protects the film or plate from light when the shutter is wound up to make an exposure. In other types of cameras with a focal plane shutter the exposure of the sensitive material is prevented by an auxiliary curtain placed in front of the shutter. This protecting curtain is wound up first and released after the shutter has been set. Such shutters are frequently termed "self-capping" since it is not necessary to cover the lens to prevent the exposure of the film or plate when setting the shutter.

With a focal plane shutter, unlike those placed near the lens, the entire image is not exposed simultaneously but successively in sections from one side to the other as the opening in the curtain passes across the face of the sensitive material. This being the case, it is evident that the image of a rapidly moving object will be distorted through movement of the image during the exposure. Such distortion commonly takes the form of elongated or compressed images, diagonally deformed; for example, wheels on rapidly moving motor cars, curved spokes in the wheels of rapidly moving machinery etc. With a horizontally moving curtain, the image is lengthened if the slit moves in the direction of the image; that is, in the opposite direction to the subject: compressed, if the slit moves in the opposite direction.

There is some variation in exposure from one side of the image to the other, due to the fact that the velocity of the curtain, starting from rest at one side of the image, increases as it passes over the film or plate until it reaches the opposite side. In well-designed shutters, however, retarding devices prevent this variation in speed from being sufficient to produce any preciptible difference in exposure.

Speed and Efficiency of Shutters.—The *speed,* or *exposure time,* of a shutter is the time interval during which light is admitted. In a between-the-lens shutter it is the time elapsing between the opening and closing of the shutter blades; in a focal plane shutter it is the time required for the slit in the curtain to pass a given spot on the sensitive material.

The actual exposure times correspond fairly well with the marked speeds on the best examples of modern between-the-lens shutters, but unfortunately the manufacturer cannot guarantee that a shutter which is reasonably accurate when it leaves his hands, will remain so, particularly if exposed to extremes of temperature, dampness or dust, or if carelessly handled. If, for any reason, the speeds appear not to correspond with the marked values, it should be placed in the hands of a competent repair man or preferably the manufacturer. On no account, should the repair be undertaken by any one not thoroughly familiar with its mechanism. On no account, should a shutter be oiled.

The *efficiency* of a shutter may be defined as the ratio between the amount of light actually reaching the sensitive material and the amount which can be admitted in the same period of exposure. A between-the-lens shutter, whose blades opened instantaneously to the maximum opening and remained open for the full period of the exposure and then closed instantaneously, would have an efficiency of 100%. In Fig. 154, are shown high speed photographs of the blades of a shutter at regular time intervals during an exposure. It will be observed that an appreciable part of the total exposure time is employed in the opening and closing of the shutter and that the full opening is available for only a portion of the exposure. The more rapid the opening and closing of the blades of the shutter, the higher its efficiency. Since the speed at which the blades open and close is approximately the same at all exposure times,[6] it is evident that the efficiency increases with the exposure time. A moment's consideration will show that the smaller the lens opening to be uncovered by the blades of the shutter, the longer the period, for a given exposure time, during which the aperture is completely uncovered and the higher the efficiency of the shutter.

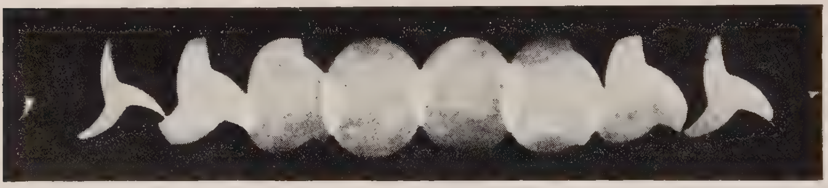

FIG. 154. Blades of a Diaphragm Shutter Opening and Closing.

Measuring the Exposure Times and Efficiency of Shutters.—The time of exposure, in the case of a between-the-lens shutter, may be determined by photographing an object moving at a known rate of speed and measuring the displacement occurring during the exposure.

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[6] An exception must be made in the case of the highest speed on some modern high-speed shutters.

GRAY—Performance Characteristics of Camera Shutters. Phot.Tech. **1** (1939) Aug. p. 14.
SALT—Some Shutter Tests. Brit. J. Phot. **72** (1925) 603.

Methods based upon photographing a revolving phonograph disk have been described frequently in the literature,[7] and less frequently the use of the wheel of an automobile (the car being jacked up), a falling body and a swinging pendulum.

Of these, the first mentioned is usually the most convenient and, under ordinary conditions, the most accurate. The turn table is first set for a convenient number of revolutions per minute and a narrow strip of paper with a heavy black line attached to it. The phonograph is then placed in a good light and exposures made of the revolving disk at the different shutter speeds. The time required for one revolution of the phonograph turn table being known (60/r.p.m.), the time of the exposure is readily determined from the portion of the circle (360°) traversed by the line on the strip of paper during the exposure.

Measurements of the efficiency of a shutter are much more difficult and require specialized equipment beyond the reach of the average amateur or professional photographer. A number of methods are described in the literature[8] all of which involve the measurement of the light passed, or the photographing of the opening in the shutter at small time intervals, on the order of 1/1000 second, throughout the period of the exposure. A useful resumé of the various methods will be found in the *Dictionary of Applied Physics.*

While in general, the efficiency of focal plane shutters is higher than diaphragm shutters the difference is not considerable if modern types of between-the-lens shutters are used as a basis of comparison.

Were it possible to have the curtain of a focal plane shutter in actual contact with the film or a plate, an efficiency of 100 per cent could be attained but this condition is manifestly impractical. The efficiency diminishes rapidly as the distance between the curtain and the film is increased and as the width of the slit is decreased. As with a between-the-lens shutter the efficiency decreases as the aperture of the lens increases.

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[7] Durham, *Brit. J. Phot.* **81** (1934) 623. Glover, *Brit. J. Phot.* **67** (1920) 417. Salt, *Brit. J. Phot.* **72** (1925) 621. Newman, *Phot. J.* **53** (1913) 219. Moore, *Brit. J. Phot.* **75** (1928) 631. Hall, *Brit. J. Phot.* **69** (1922) 323. English, *Amer. Phot.* **33** (1939) 877.

[8] Andersen, *Dictionary of Applied Physics,* Vol. **4**, 670. Andersen, *Trans. Opt. Soc.* (London) **22** (1920) 161. Nutting, *Phot. J.* **56** (1916). Eyles & Selwyn, *Proc. Phys. Soc.* (London), **47** (1937) 447. Blair & Long, *Phot. J.* **74** (1934) 423. Gray, *Phot.Tech.* **1** (1939) Aug. p. 14. Andersen, *Brit. J. Phot.* **76** (1929) 667, 682, 698.

With a focal plane shutter, the maximum efficiency at high speeds will be obtained by using as wide a slit and as high a spring tension as possible rather than a narrow slit at a lower tension.

Finders.—The finder is a very important feature of hand cameras since it provides the only means of knowing what will be included in the picture. The first requirement of a finder is that it should indicate exactly the area included by the lens of the camera. This is possible for all distances of the subject only if the axis of the finder and the lens coincide, a condition which is obviously impossible except in a reflex camera where the camera lens is used as a finder.

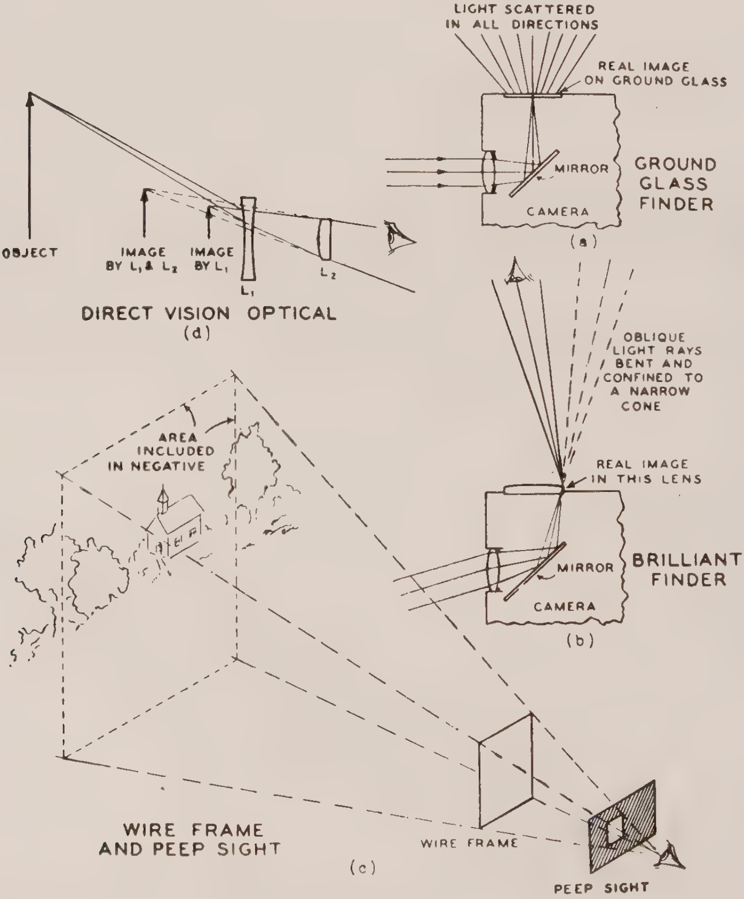

Fig. 155. Finder Systems.

In designing a camera, the errors resulting from the separation of the finder and the lens are kept as small as possible by placing the finder as close to the lens and by making the axis of the one intersect with that of the other at a distance of approximately 15 feet. The difference in finder and lens image is then insignificant except on nearby subjects. In some cases, the field of the finder is made smaller than that of the lens so that all of the image seen in the finder will be included in the negative regardless of the distance of the subject.

The simplest form of reflecting finder consists essentially of a miniature box camera as shown in Fig. 155 with a mirror placed at an angle of 45° behind the biconvex lens to reflect the image to the ground glass screen. The so-called "brilliant" finder is similar except that the ground glass screen is replaced by a second lens which results in a clearer and more brilliant image, since the light is not scattered by the ground glass.

In all reflecting finders, the image is erect, but reversed laterally, i.e., from right to left. This is true also of the image seen on the focusing screen of a reflex or twin-lens camera.

Direct vision finders are of several types. One of the simplest is known as the wire-frame, or iconometer, finder. It consists of a metal frame corresponding to the picture size and a deep-sight; the first mentioned is placed in the same plane as the lens and the latter in that of the plate or film.

In some cases, the front frame is made considerably smaller than the picture area and its distance from the peep-sight reduced so that the angle included will correspond with that of the camera lens. This enables the finder to be placed on the side of the camera.

In still another type of direct vision finder the front frame consists of a negative lens which forms a virtual image of the subject. The size and power of the lens determine the size of the field included in the finder.

Today, in finders of this type, the peep-sight is usually a low-power positive lens which projects the virtual image formed by the negative lens to a more comfortable viewing distance from the eye. This optical system results in an image which is not only erect but is also not reversed from right to left. Finders of this construction are very common on current miniature cameras.

Focusing Scales.—All focusing cameras, except those having a ground glass or range finders coupled to the lens, must be focused by scale. In the case of a camera in which the entire front moves, the focusing scale is usually attached to the camera bed. In models with a self-erecting front which are focused by means of the front element of the lens, the scale is ordinarily on the circumference of the lens element or the face of the shutter.

The positions on a focusing scale may be calculated from the following formula:

$$\text{Scale interval from the infinity point} = \frac{F \times F}{S - F}$$

where F = the focal length of the lens
S = the distance of the subject focused on.

The same units (inches or centimeters) must be used throughout.

The accuracy with which the focusing scale must be calibrated increases with the focal length and the relative aperture of the lens.

Range Finders.—Range finders are used with cameras focused by scale to measure the distance of the subject and thus determine the proper setting on the focusing scale. Connecting the range finder mechanically with the camera lens for all practical purposes, converts the instrument from a distance measuring device to a means of accurately focusing the camera on the desired object. Coupled range finders make possible direct, accurate and convenient focusing and were first employed on miniature cameras but are now found on cameras of larger size, particularly those designed for press photography. In many cases, however, the mechanical coupling device leaves much to be desired from the standpoint of accuracy, the shortcomings being particularly serious on nearby objects.[9]

The range finders fitted to cameras, or sold separately as an accessory, are based upon the same general principle of triangulation as those designed for military use.[10]

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[9] Schwalbe, *Phot.Tech.* **1** (1939) Nov. p. 14.

[10] Other types of distance measuring devices include: (1) instruments of the telescopic type in which the distance is measured from the extension necessary to obtain a sharp image of the object, and (2) instruments measuring distance in terms of the variation in the apparent size of a standard object with distance. See Lockett, Telemeters and Their Use. *Brit. J. Phot.* **74** (1927) 149.

A range finder designed especially for use in dim light where the usual type of range finder is difficult to use, has been placed upon the market (Focus-Spot). An incandescent lamp operated from flashlight batteries is placed in the plane of the sensitive material. An image of this filament is projected on the subject by a lens which is placed directly above the camera lens and has the same focal length. Consequently, when the image of the filament on the subject is sharp, the camera lens also will be accurately focused for the same plane.

Consider two rays of light from a very distant object *E*, coming through two openings *O* and *P*, Fig. 156.[11] Because the object *E* is very distant, these two rays are parallel and pass through *A* and *B*. Now consider a close object *D*, situated on the ray passing through *O*.

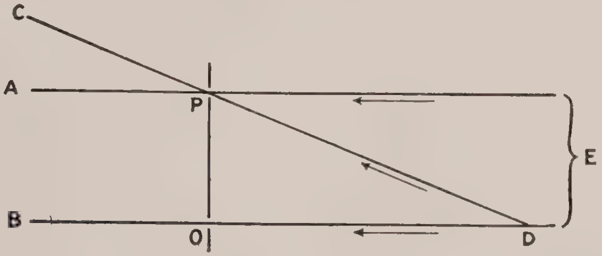

Fig. 156.

The ray from *D* passing through *O* will also pass through *B*, but the ray from it passing through *P* will not pass through *A*, but through *C*. The closer *D* is to *O*, the greater will be the distance of *C* from *A*. The opening *P* can now be moved toward *O*, or if some adjustable device is provided at *P* to bend the ray from *D* to go through *A*, the amount of adjustment needed to accomplish this can be made to measure the distance from *O* to *D*. It would be difficult to know just when *C* is moved the correct amount, unless there were something with which

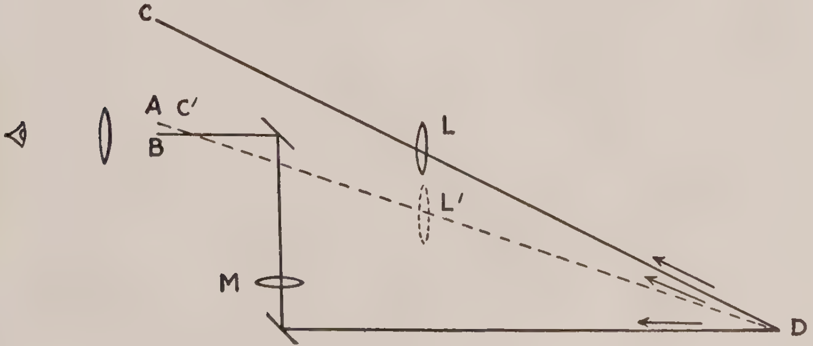

Fig. 157.

to compare it. A fixed point for comparison is provided by moving *B* over to the original position of *A*, by reflecting the beam twice, Fig. 157. Thus *B*, and *C* when adjusted to *C′*, are presented to the eye together, and any difference in their positions is readily seen.

[11] *Kodak Reference Manual*, Eastman Kodak Company.

Range finders may be divided broadly into two types: (1) those in which a part of the image is movable (split-field) and (2) those in which two complete images are produced (superimposed or coincident image), one of which is movable. In both cases, the distance of the object is measured by moving the displaced image, in the split-field type until it coincides with the fixed portion and in the other case until the two images merge to form one (Fig. 158).

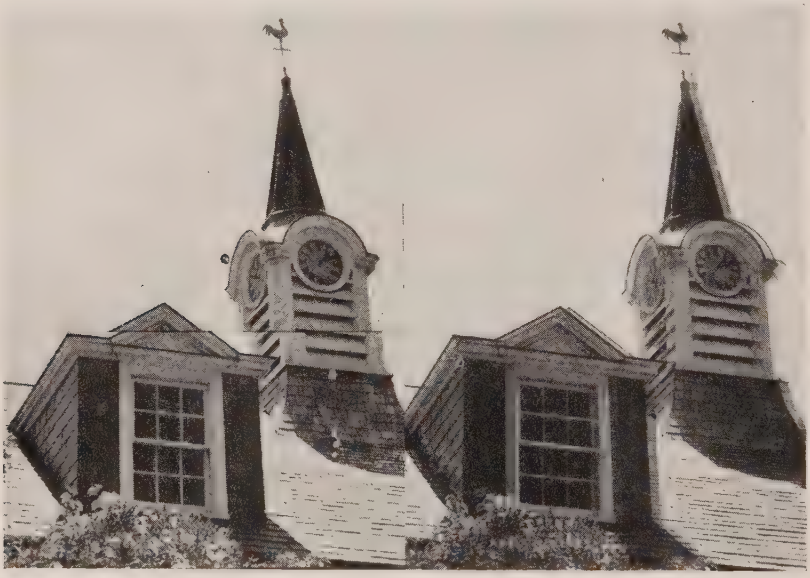

Fig. 158. Illustrating the Appearance of the Image in (left) a Split-Field Range Finder and (right) in a Coincidence Range Finder.

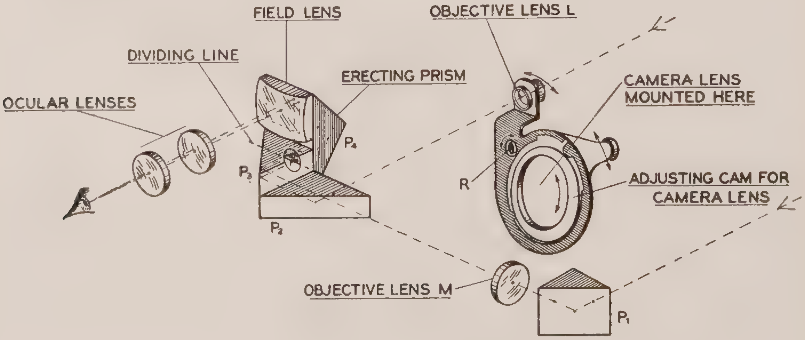

Fig. 159.

Range-Finders of the Split-Field Type.—In Fig. 159,[12] *B* and *C* are images of the same object *D*, created by two lenses, one of which is *L*, and the other *M*. To make *C* coincide with *B*, lens *L* is moved to the position *L′*. The closer *D* is, the more *L* must be moved.

The objective lens, *L*, in this camera is carried on a movable support actuated by the adjusting cam, which is turned by the focusing knob. Turning this knob moves the camera lens along its axis, and thereby focuses it, by means of a helical thread. This cam is so computed that, when the range finder objective *L* is correctly placed for a given object, the camera lens is focused on this object.

The two images created by lenses *L* and *M* occur on the face of prism P_4 (Fig. 159), at the common boundary of prisms P_2 and P_3. The rays from *M* travel above prism P_2, the rays from *L* travel inside prism P_2 and are reflected at a point just below the other rays. Both rays are then deflected by prism P_3 back to form the split image. P_4 is an erecting prism, the purpose of which is to present the images to the eye right side up. The field lens collects the rays forming the image and the ocular lenses are provided so that the images, which are only a short distance from the eye, may be seen easily.

Range Finders of the Superimposed Image or Coincidence Type.—In the example shown in Fig. 160,[13] the knurled knob *F* is moved in

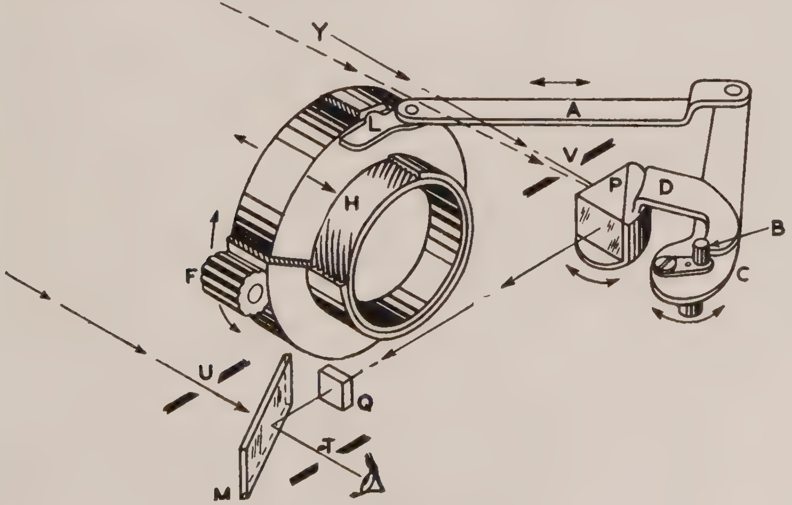

Fig. 160.

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[12] This construction is employed on the Kodak Bantam Special.

[13] Kodak Retina II. This description is from the *Kodak Reference Manual.*

the direction indicated by the arrows. This rotates the outer shell of the lens mount, and the lens and shutter mounting is moved in or out on the helical threads. The range finder system is coupled to the lens and shutter mount by lug, *L,* which is fastened rigidly to the shutter casing, and the link arm *A.* As the lens and shutter is moved in and out, the cam *C* swings about a vertical axis and the pin of the bearing *B* also swings causing the lever *D* and hence the prism *P* to swing about a vertical axis which is directly under the rear or reflecting surface of the prism. As the prism swings through a small angle, the convergence of the two rays, *X* and *Y*, entering the range finder is changed so that the point of convergence is the point for which the lens is focused. The light ray *Y* enters the finder at the aperture *V,* is reflected at the rear surface of the prism *P* through the filter *Q* to the plane glass plate *M,* is reflected at the glass surface, and passes through the aperture *T.* The light ray *X* enters the finder at the aperture *U* and passes through the glass plate and through the aperture *T.*

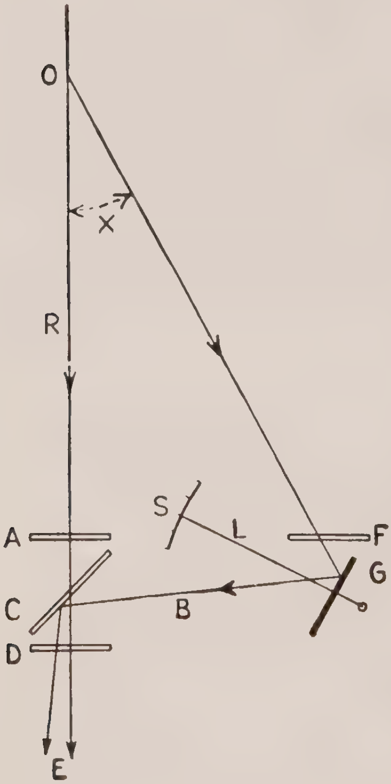

Fig. 161.

When the eye is placed close to the aperture *T,* two images are seen. One is large and colorless, and the other is smaller, tinted a light orange (by virtue of the small filter placed at *Q*), and is located in the center of the larger image. When the object is in focus, the two images (i.e., the clear and the colored) in the range finder coincide. This type of range finder is very simple and objects before the camera are seen natural size in the range finder.

Leica Coupled Range Finder.—The principle of the range finder fitted to Leica 35 mm. cameras may be seen from Fig. 161.[14]

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[14] Cornog, *Amer. Phot.* (1937) Jan. p. 1.

" A ray of light from the object at *O* passes through the window *A*, through the glass sheet *C*, which is set at an angle of 45° to line *OA*, through the window *D*, and into the eye at *E*. Another ray of light from the same point on the object passes through window *F*, is reflected from mirror *G*, then from the glass sheet *C*, and finally passes through window *D* into the eye at *E*. Thus the eye at *E* will see two images, one direct and brilliant, the other, much weaker, reflected from the mirror, *G*. The mirror *G* can be rotated about an axis *H* by means of lever *L*, and it is obvious that if this mirror *G* is rotated to the proper position, the ray of light *OGC* will then emerge from window *D* along the line *OE*, and the two images will seem to have become one, or are coincident. Corresponding to this proper position of the mirror *G*, the end of the lever *L* indicates on the empirically calibrated scale *S* the distance *OC*, which is called the 'range' of the object at *O*."

Zeiss Coupled Range Finder.—The type of range finder employing two mirrors, or prisms, one fixed, the other movable, has the disadvantage that the distance through which the moving mirror, or prism, must move in measuring objects at distances from infinity to about three feet, is considerably less than the distance which must be traversed by the lens in its focusing mount. This increases the difficulty of accurate coupling, since a small error in the coupling mechanism will introduce large errors in focusing. To avoid this, a different type of range finder employing circular, rotating prisms has been developed by Zeiss Ikon for the *Contax*. The optical system is shown diagrammatically in Fig. 162.

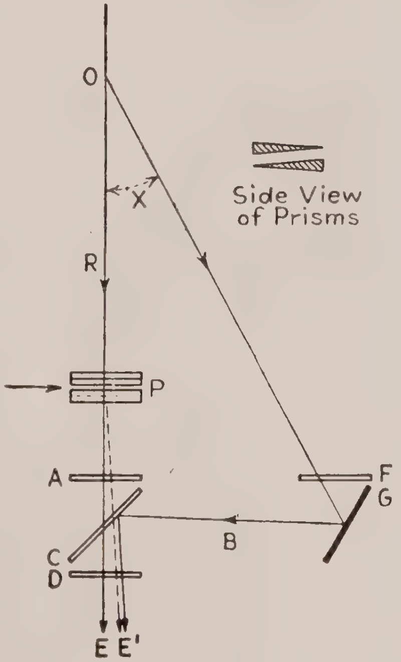

Fig. 162.

" At *P'* there are two prisms of triangular cross section and very small angle. Viewed in the direction of the arrow, these prisms would look like the inset in Fig. 162. In the figure these prisms are shown in such a position that a ray of light such as DF will pass through them without any change in direction, and the ray would go along the line OE into the eye at E; together they act here like a sheet of glass with parallel faces. These prisms are arranged so that they will rotate about the line DFE in opposite directions and at equal rates as the focusing device of the camera is adjusted. Having been turned for a little way the pair no longer act like a sheet of plane parallel glass, but like a single prism, since now one side of the combination is thicker than the other. This can easily be demonstrated by using the pointed ends of two lead pencils to represent the prisms, holding the pencils perpendicular to the plane of Fig. 162 and rotating each towards the right-hand side of the figure in opposite directions. The result is that the ray of light is caused to deviate from the path DFE to the path DFE'. In this case, mirror G is fixed, as is the sheet of glass C, so that the ray OGE' passes into the eye at E'. It is obvious that by rotating the prisms as described, the two images can be brought into coincidence along the line FE'.

Tripods and Camera Stands.—A tripod should be used for all exposures longer than 1/50 second with miniature cameras and 1/25 second with larger cameras. Movement of the camera during the exposure is particularly to be avoided with the miniature camera owing to the high degree of enlargement. The most important requirement of a tripod is stability; unless it provides a firm support for the camera, it is worthless. An important factor in stability often overlooked is the head or camera platform, which should be free from "loose play" and large enough to provide adequate support for the camera. The legs also should be rigid and should slide or fold easily. The tightening screws should be large. Nothing is more exasperating than fussing with small, tight thumbscrews in cold weather. The tripod should preferably be high enough to permit the use of the camera at eye level and still provide a base sufficient to prevent the camera from being readily tipped or blown over. The legs of some tripods are fitted with interchangeable tips: a sharp steel point for use on soft surfaces and a rubber tip for use on polished surfaces.

A tilting head is a very desirable feature of many tripods or can be purchased separately. In selecting a tilting top, as in selecting a tripod, one should look first for stability—and secondly, for convenience in use. Weight does not necessarily mean stability but rigidity is seldom had in light-weight equipment. In particular, one should make sure that the tilting top provides sufficient clearance for the camera when tilted to a reasonable angle up or down.

Tripod braces may serve to prevent damage to the camera when using a tripod on marble floors or other smooth surfaces.

In Fig. 163 is shown a type of tripod, or folding stand, preferred by many home portrait and commercial photographers. It is more rigid than the usual form of tripod, does not slip on polished surfaces and is not as easily upset. Its disadvantages are the great weight and bulk.

Lens Shades.—It is gratifying to see that lens shades, neglected for so many years by both manufacturers and photographers, are again coming into general use. With modern, large-aperture lenses, the use of a lens shade is advisable at all times if negatives of the maximum brilliance are to be expected. The ideal lens shade would prevent all light reaching the lens except from that part of the subject included in the picture. For the most part, the lens shades available commercially, being cylindrical in shape and of fixed length, do not by any means approach this ideal condition; nevertheless they do prevent a great deal of extraneous light from reaching the lens and are highly desirable.

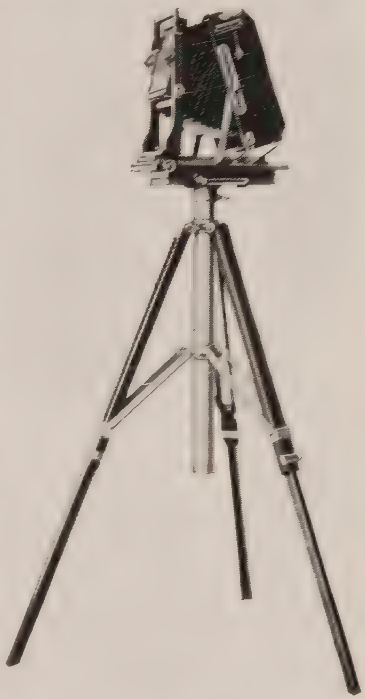

Fig. 163. Folding Camera Stand.

In many cases, the lens shade is designed to serve also as a filter holder. This is an advantage in that it eliminates another accessory which may be lost, misplaced or forgotten.

Plate and Sheet Film Holders.—Hand cameras of foreign origin for plates and cut film generally employ single metal holders shown in Fig. 164. A pressure plate behind the hinged metal frame makes the holder suitable for both cut film and plates.

The typical American style double holder is shown in Fig. 165. Lifting up the hinged flap at the bottom allows cut film to be slipped in the grooves along each side of the holder. Glass plates are held in position by overlapping portions of the flap and the stays at the top of the holder.

Plate or film holders designed for three-color cameras differ from those designed for black and white photography in the provisions made to ensure accurate registration and for keeping the sensitive material flat when film is employed. Usually some variation of the book-type is employed, the holder being loaded from the back which acts as a pressure plate to maintain the sensitive material in the desired plane.

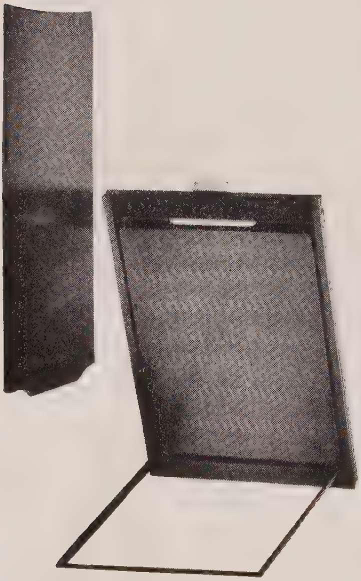
Fig. 164. Single Metal Plate and Film Holder.

Roll Film Adapter.—Roll film can be used with many cameras designed for cut film, film pack or glass plates, through the purchase of a *roll film adapter.*

Film Pack Adapters.—Film packs are now used exclusively in film pack *adapters,* a book-form, light-tight holder with a removable slide similar to a film holder which enables the film pack to be removed from the camera so that the image may be focused on the ground glass.

Lens Adapter.—The lens adapter shown in Fig. 166 enables lenses to be changed readily on view, commercial and studio cameras. The steel diaphragm firmly grips the lens where the flange screws on and holds it securely. An adapter of this

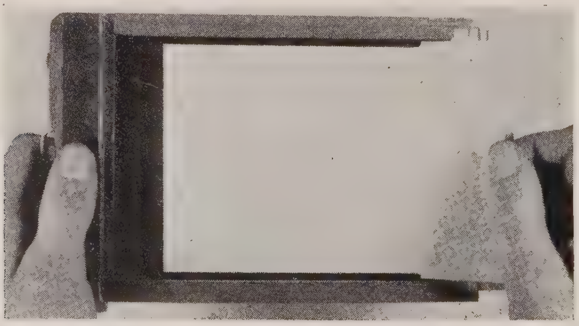
Fig. 165. American Type Sheet Film Holder Showing Method of Loading.

type is instantly adjustable to fit different sized lenses and does away with the need for more than one lens board.

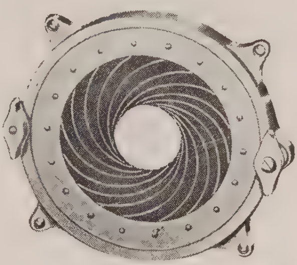

FIG. 166. Adjustable Lens Board.

Plate and Cut Film Magazines.—Plate or cut film magazines provide the means of making a number of exposures on glass plates or cut film without the necessity of having an equal number of plate or cut film holders. In a familiar type (Graflex) plates or sheet films are loaded in thin metal septums and inserted in the magazine in a darkroom. A slide similar to that of a plate or cut film holder is withdrawn before the exposure. After the exposure, the septum containing the film is withdrawn from the front of the magazine next to the slide into the light-tight leather bag at the end by means of a sliding lever, and transferred by hand to the rear of the magazine, thus placing the second septum and its plate or film in position for the exposure. Numbers on the back of the thin metal septums provide a record of the exposures.

Changing Bags.—Changing bags enable film or plate holders, or developing tanks, to be loaded in daylight, when a darkroom is not available. The holders are slipped into the end of the bag which is then closed. The hands are next inserted through the sleeves which have rubber wrist bands to keep out the light.

Reducing Backs permit the use of smaller film or plate holders with view, commercial or studio portrait cameras.

Self-timers are incorporated in some between-the-lens shutters, such as the Compur, or are available separately as an accessory. The self-timer delays the operation of the shutter by means of clockwork mechanism or an air escapement device, and enables the picture maker to include himself in the picture. In some models, the timing system may be used to make automatically timed exposures.

Focusing magnifiers not only enlarge the image but increase its brilliancy and thus enable the image on the ground glass screen to be focused with greater accuracy. They are especially useful when photographing interiors or other dimly lighted subjects.

Diffusion disks formed of ruled, molded or matted glass or embossed celluloid are supplied for use over the lens to soften the definition of fully corrected lenses. The diffusion produced is not of the same character as that produced by semi-achromatic lenses, but for some subjects may be an improvement over the sharp definition of a fully corrected lens.

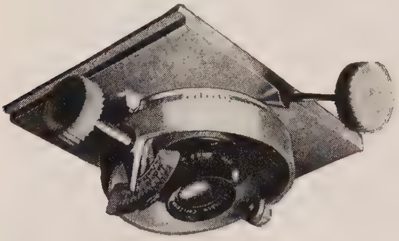

FIG. 167. Tilting Lens Holder.

In some cases, a number of disks producing varying degrees of diffusion are available, in other cases the degree of diffusion is controlled by the diaphragm.

Swing Lens Mount.—In Fig. 167 is shown a lens mounting which performs the same function as a swinging camera front. It is obviously suitable only for view, commercial or studio portrait cameras.

Stereo Attachment.—The Stereo attachment shown in Fig. 168[15] enables stereoscopic pictures to be made with some single lens cameras simply by placing the stereo attachment over the lens of the camera.

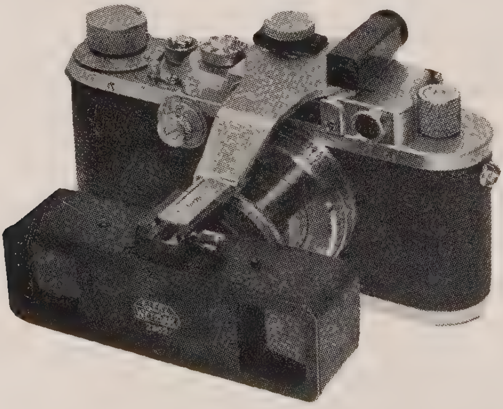

FIG. 168. Stereo Attachment. (E. Leitz & Co.)

The two prisms present to the camera lens two images of the subject which are substantially the same except for the difference in viewpoint, which is approximately 70 mm. (2¾ inches). The camera lens images these reflected images on the film to produce two pictures side by side, constituting a stereoscopic pair.

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[15] E. Leitz, New York.

CHAPTER V

LIGHT SOURCES

Light Sources.—The chief sources of radiant energy producing light are bodies or gases heated to the point of incandescence. The light of the sun, for example, is due to masses of hot gas under high pressure. In the tungsten lamp, a filament of tungsten, and in the arc, carbon, are heated to the point of incandescence by the resistance offered to the passage of the electric current. In gaseous conductor tubes, such as neon or sodium lamps, light is produced from the conduction of electricity through gas. The current breaks down the molecules of the gas producing radiation, usually in both the visible and invisible regions of the spectrum. The fluorescent lamps, now gaining in popularity both for general illumination and for photography, make use of still another means of producing light, that is by fluorescence. A comparatively large number of substances, both organic and inorganic, have the property of giving off light, or becoming fluorescent, when exposed to radiation of suitable wave length, usually beyond the visible region. Generally, fluorescent substances absorb ultra-violet energy and re-radiate it at longer wave lengths, which are visible to the eye as light.

Light and Illumination.—The relation between light and illumination is that of cause and effect; light is the cause and illumination the effect. Brightness is illumination as modified by the reflectivity of the surface illuminated.

The *intensity* of a source of light is expressed in candle power. Thus, a light source whose intensity is one hundred times as great as that of the standard candle adopted as a unit of measurement, is said to be a light of 100 candle power. The candle power of a light source, however, does not necessarily indicate the total quantity of light radiated by that source. A 21 candle power automobile headlight lamp, for example, may produce a light beam equivalent to 1000 candle power through the concentration of the light emitted by the lamp, originally emitted in all directions, into a single directed beam.

The *quantity* of light is called the *lumen*. It is equivalent to the quantity of light on a surface of one square foot, every point of which is at a distance of one foot from a light source of one candle power.

The illumination on a surface is expressed in either foot candles or meter candles. A foot candle represents the illumination equivalent to that produced at a *point* on a surface at a distance of one foot from a light source of one candle power. A meter candle is similar except that a distance of one meter is substituted for one foot.

Brightness is measured either in foot candles of reflected light, in Lamberts, the latter being equivalent to one lumen of reflected light per square centimeter, or in foot lamberts which represents one lumen of reflected light per square foot.

Spectral Energy of Light Sources—Color Temperature.—The wave lengths present in the source of radiant energy and the variation in the amount of energy with the wave length, or as it is called, the distribution of spectral energy, is an important characteristic of a light source for photographic purposes. The spectral energy characteristic of a light source may be represented in two ways: (1) *A spectral energy curve* in which the intensity of the radiant energy for any particular wave length is plotted on the vertical axis against the wave length (Fig. 169), or (2) by the *color temperature* which may be defined as

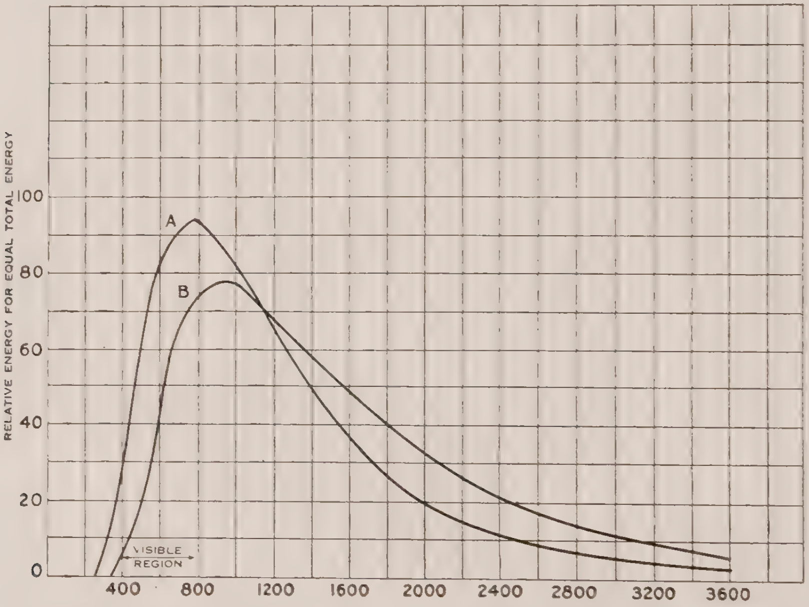

FIG. 169. Spectral Energy Curve of Incandescent Tungsten Radiation.

the temperature to which a black body must be heated to produce light having the same integral color as the source under consideration. For example, if the light from a tungsten lamp is referred to as having a color temperature of 3200° K., it means that the light of the lamp has the same spectral distribution as a black body at a temperature of 3200° K. Only the spectral energy characteristics of a source having a continuous spectrum, however, can be expressed in terms of color temperature.

The spectral energy characteristics of a number of light sources in terms of the equivalent color temperature, is shown in the following table:

Clear blue northwest sky	20,000° K.
Blue sky, thin white clouds	12,000° K.
Blue sky	10,000° K.
Overcast sky	6,000° K.
Sunlight, average noon	5,400° K.
Sunlight, one hour after sunrise	3,500° K.
Gas filled incandescent tungsten lamp (average)	3,000° K.
Carbon type incandescent lamp	2,080° K.
Standard candle	1,930° K.

Measurement of Color Temperature.—All methods of measuring color temperature which are practical for the average photographer are based upon subjective rather than objective operation. They are consequently subject to error arising from variations in the color sensitivity of the eye of the user. Persons wholly, or even partially color blind, for example, are unable to make accurate measurements of color temperature with the available equipment, while considerable skill and experience are required of the person with normal visual response to color. Of the three methods of measuring color temperature, the only one really practical for the photographer is that involving the use of a color meter of which there are two examples (Fig. 170).

In these, two images of the subject are seen, one through a monochromatic filter, the other through a dichroic (two colored) filter. These two fields are made to match by a wedge which controls the transmissions of the two filters.[1] The wedge is calibrated in color temperatures so that, when the transmissions of the two filters have been equalized, the effective color temperature of the source is indicated on the dial of the instrument.

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[1] Lowry and Weaver, *J. Soc. Mot. Pict. Eng.* **32** (1939) 298.

Sunlight.—The intensity of the light from the *unobscured* sun depends upon its distance above the horizon which in turn is dependent upon (1) the latitude, (2) the hour of day, and (3) the time of year.[2] Usually the light of the sun is supplemented by that reflected from the sky. In the absence of clouds, about 1/5 of the total illumination consists of skylight, or sunlight, scattered by the atmosphere enveloping the earth. The proportion of skylight to sunlight increases with clouds. Obviously, when the sky is completely overcast, there is no direct sunlight and all light is sky light.

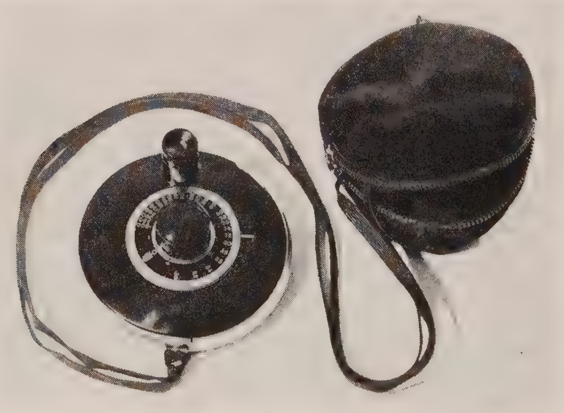

FIG. 170. Color Temperature Meter. (Eastman Kodak Company.)

The intensity of sunlight depends also to a large degree upon atmospheric conditions and, so far as photographic exposure is concerned, the variations due to clouds, and less frequently other atmospheric disturbances—such as dust and water vapor, are probably more serious than those arising from the position of the sun above the horizon. The effect of such variations cannot be accurately determined by the unaided eye, but only with the aid of actinometers or photometric apparatus. (See Chapter 17, Exposure.) Exposure tables and calculators employ such descriptive terms as intense sunlight (no clouds), (1); light clouds (shadows barely visible), (2); cloudy bright (no shadows but bright), (3); heavy clouds, (4); and very heavy clouds, (5 or more). The numbers represent the relative intensity of sunlight under the conditions described. Obviously, these are only approximations and depend to a large extent upon individual judgment.

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[2] This subject was first fully investigated by Bunsen and Roscoe, whose work has been repeated several times with improved apparatus. Kimball, *Trans. Ill. Eng. Soc.* (N. Y.) **18** (1923) 457.

Of equal concern in color photography is the effect of such variations on the spectral energy distribution, or effective color temperature, of sunlight. Reliable data on the subject are apparently very meager. The following table contains values for average color-temperature of sunlight for various seasons and weather conditions, as determined by A. H. Taylor of the General Electric Lamp Laboratories.[3]

AVERAGE COLOR-TEMPERATURES OF DAYLIGHT FOR VARIOUS SEASONS AND WEATHER CONDITIONS
(LIGHT RECEIVED ON A HORIZONTAL PLANE)

	April and May	*June and July*	*Sept. and Oct.*	*Nov., Dec. and Feb.*
Direct sunlight alone, 9 a.m. to 3 p.m.	5800° K.	5800° K.	5450° K.	*5500° K.
Direct sunlight before 9 and after 3	5400	5600	4900	*5000
Sunlight plus light from clear sky				
9 a.m. to 3 p.m.	6500	6500	6100	*6200
Before 9, after 3	6100	6200	5900	*5700
Sunlight plus light from a hazy or slightly overcast sky	5900	5800	5900	5700
Sunlight plus light from 25% to 75% overcast sky	6450	6700	6250	....
Totally overcast skylight	6700	6950	6750	....
Light from hazy or smoky sky	7500	8150	*8400	7700
Light from clear blue sky				
9 a.m. to 3 p.m.	26,000	14,000	12,000	*12,000
Before 9, after 3	27,000	....	....	12,000

* One observation.

Incandescent Tungsten Lamps.—The incandescent tungsten lamp consists essentially of a drawn filament of tungsten in a glass globe containing argon and nitrogen. The energy required to force an electric current through the filament raises its temperature to incandescence. The operating temperature in the case of the average, modern, high-efficiency lamp is in the neighborhood of 5500° F. The filament is consumed but slowly despite this temperature because it is surrounded by inert gases which do not combine chemically with it and retard evaporation.

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[3] *Trans. Ill. Eng. Soc.* **25** (1930) 154.

The radiation emitted by the incandescent tungsten filament is continuous from the near ultra-violet, through the visible region and into the infra red, the extreme limits being between 400 and 3600 millimicrons[4] (Fig. 169). Thus, only a small portion of the total radiation from an incandescent tungsten lamp lies in the visible region; from 75 to 80% of the wattage input is emitted as infra-red radiation. The greater part of the radiation in the infra-red region is in the near infra-red extending from the limit of the visible region to about 5000 millimicrons. Incandescent tungsten lamps are, therefore, an excellent source of radiation for infra-red photography as well as for work in the visual region.

The spectral characteristic of the radiation emitted by any particular type of incandescent tungsten lamp depends upon the voltage at which it is operated, and is most conveniently expressed in terms of its equivalent color temperature. The maximum filament temperature in degrees Kelvin, corresponding to the color temperature, for some of the lamps commonly employed for photographic purposes, is as follows:

Lamps	*Watts*	*Volts*	*Bulb*	*Maximum True Temperature (Degrees K.)*
General Service	500	115	PS-40	2935
General Service	1000	115	PS-52	3000
General Service	1500	115	PS-52	3020
(Movieflood)	2000 C.P.	115	PS-52	3380
Projection (Monoplane)	500	115	T-20	3265
Photoflood No. 1	250	115	A-21	3490
Photoflood No. 2	500	115	A-25	3430
Photoflood No. 4	1000	115	PS-35	3410
Photoflash				3500 (Average color temperature)

Increasing the operating temperature of the filiament, i.e., the voltage applied, (1) increases the light output, (2) the effective color temperature, and (3) shortens the life of the lamp. The effect of increasing the voltage applied to a typical tungsten lamp from 95 to 125 volts is shown in Fig. 171.[5] It is important, therefore, to operate incandescent tungsten lamps at their rated voltage, if the proper results are to be obtained. If the voltage is not constant, both the intensity and the

[4] Forsythe and Worthington, *Astrophysical J.* **72** (1925) 146.

[5] Forsythe, *Phot.Tech.* **1** (1939) June p. 21.

color temperature will vary. Variations in either intensity or color temperature affect exposure, although ordinarily the errors due to such variations is within the exposure tolerance of the negative material.

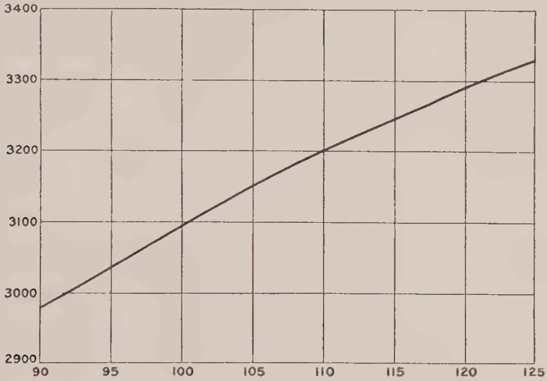

FIG. 171. Effect of Variation in Voltage on the Color Temperature of a Typical Incandescent Lamp.

In the case of color photography, however, variations in color temperature are serious because most color processes are usually adjusted for light of a particular color temperature. Professional Kodachrome, for example, is balanced for a color temperature of 3200° K. and it has been stated that a variation in color temperature of 50° K. is evident in the finished result. If this is correct, the permissible variation in voltage in color photography is only a few percent, being approximately 2.5% for a lamp having an effective color temperature of 3200° K. on a 110 volt circuit.

It is evident, therefore (1) that the voltage on the lamp must be known, and (2) that means must be provided to keep fluctuations in voltage within the allowable limits. The first requirement is easily met by the installation of an accurate volt meter. Voltage regulating devices may be divided into two types: (1) those manually operated, and (2) those which are automatic in operation. The latter are naturally the more convenient, but are rather expensive in the sizes required for studio lighting equipment. Smaller units are excellent for use with printers, enlargers, etc. Manually operated variable transformers answer nearly every requirement in the studio and at a much lower cost.[6]

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[6] Dudley, Measuring and Controlling Light for Color Photography. *Phot.-Tech.* 1 (1939) Oct. p. 8.

Both the luminous intensity and the effective color temperature of an incandescent tungsten lamp become less with age. The decrease is naturally more rapid in short-life lamps, such as the Photoflood, than in lamps operated at a lower filament temperature and designed for a longer useful life. The change in color temperature is, in general, of importance only in color photography. In Fig. 172 is shown the effect of continued operation on the color temperature of a typical incandescent lamp.[7]

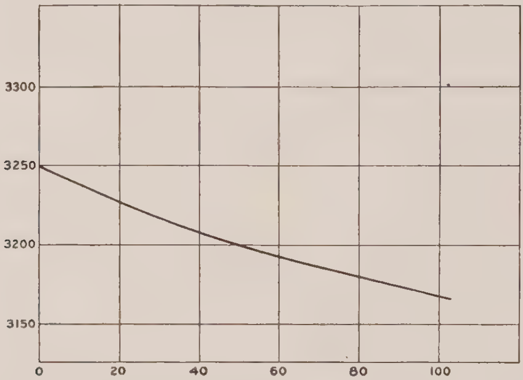

Fig. 172. Curve Showing the Relationship Between Color Temperature and Age (Hours of Operation) of a Typical Incandescent Tungsten Lamp.

Gaseous Conductor Lamps.—Lamps of this type consist of a tubular bulb with an electrode in each end, the tube being filled with gaseous sodium, neon, mercury or another suitable element. When a current of suitable voltage is applied, the flow of current produces an arc, and light is produced as a result of electronic displacements within

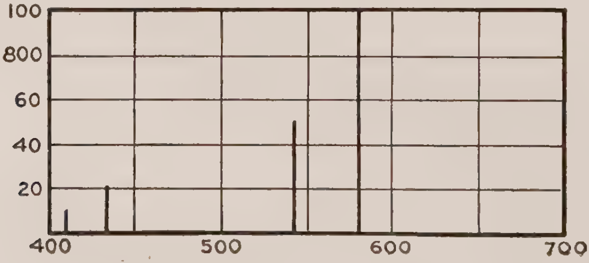

Fig. 173. Spectral Energy Distribution of the Mercury Vapor Lamp.

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[7] Forsythe, *Phot.Tech.* 1 (1939) June p. 21.

the atomic structure of the gas. While the sodium and neon lamps are probably the best known lamps of this type today, the mercury vapor, or Cooper-Hewitt lamp, was the first to be introduced commercially and, until recently, the only one whose characteristics rendered it suitable for general photography. The spectrum of gaseous conductor lamps is not continuous, but consists entirely of a few bright lines in widely separated parts of the spectrum (Fig. 173). The spectrum of the mercury vapor lamp, for example, is confined to a few bright lines in the violet, blue and green. Lamps of this type, therefore, are not suitable for use with color sensitive materials in the photography of colored objects.

In the case of the mercury-vapor lamp, however, the relatively high emission in the violet and blue renders it especially suitable for use with blue sensitive materials, and its low current consumption, high degree of diffusion and low operating temperature adapt it to contact and projection printing, blueprinting, exposing rotogravure and other pigment papers and the copying of black and white originals in photo-engraving and other photo-mechanical reproduction processes.

The fluorescent lamps now coming into general use may be regarded as a development of the mercury-vapor lamp, since they employ the same basic principle. In the mercury-vapor lamp, however, the electrical characteristics, the vapor pressure and voltage are regulated so as to produce directly as much light as possible. In the fluorescent lamp, these elements are adjusted so that the discharge produces little visible light, but has a high emission of energy in the ultra-violet near a wave length of 253.7 mμ. The inside of the bulb is then coated with

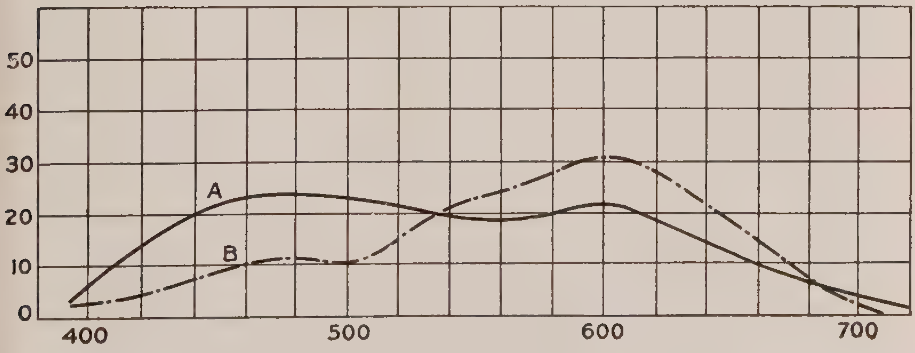

FIG. 174. Spectral Energy Curves (*a*) Daylight and (*b*) White, Fluorescent Lamps.

fluorescent powders, which become luminous when exposed to ultraviolet radiation. Various colors are obtained by using different fluorescent or phosphorescent powders. The daylight, white and blue lamps are those of chief interest to photographers. The daylight lamp, as its name indicates, approximates daylight (Fig. 174) and may be used to supplement daylight, or alone where a light source of daylight quality is required. The white lamp corresponds approximately with high efficiency tungsten-filament lamps with respect to the color of the light.

Nearly all the light of the blue lamp is in the blue-violet region; it is, therefore, well adapted for contact and projection printing, and other work in which blue sensitive materials are employed. A point of some importance is that the color of the light produced by fluorescent lamps, unlike that of incandescent tungsten filament lamps, does not vary appreciably with variations in line voltage; there is no need, therefore, for voltage regulating devices.

The tubes operate at a temperature of approximately 120°. The low operating temperature, high photographic efficiency and freedom from disturbing glare, make the fluorescent lamp ideal for portraiture and many other branches of photography. Because of its shape, the fluorescent lamp is well adapted for general floodlighting, when used in trough reflectors. Being extended sources, fluorescent lamps have very little "carrying power," i.e., candle power in a given direction, and cannot produce a beam of light of high intensity as required for spotlighting. For such requirements, incandescent tungsten filament lamps must be employed.

Unlike tungsten-filament lamps, fluorescent lamps require auxiliary control equipment. This control equipment consists (1) of an iron core choke coil which limits the arc current, and (2) a starting switch which momentarily closes and then opens the electrode heating circuit. Each lamp requires a separate auxiliary, although the equipment for two or more lamps may be in a single container.

Arc Sources.—Before the widespread use of panchromatic materials, the electric carbon arc was widely used as a source of light for photographic purposes, because of its high intensity and the abundance of light in the region of the spectrum to which blue sensitive materials are sensitive. Even today, the arc is widely used in photo-mechanical

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Engineering Data on Fluorescent Mazda Lamps. Engineering Dept., General Electric Co. 1940.

WORSTELL—Modern Photographic Light Sources. J. Phot. Soc. Amer. **6** (1940) 4.

processes, blueprinting and in other operations in which blue sensitive materials of comparatively low sensitivity are employed. For general photography, the electric arc has been falling into comparative disuse in recent years, because of the greater popularity of incandescent tungsten lamps, which are cleaner, more constant, require less attention, emit no fumes and in general are better adapted to the requirements of flood or general lighting.

Ordinary carbons are less frequently employed today for photographic purposes than the *white flame* or *panchromatic* carbons produced by drilling the carbon and filling the core with inorganic salts selected either for the purpose of increasing the intensity of the light emitted or modifying its spectral distribution. The incorporation of rare earth fluorides, for example, as in the so-called white flame carbons, results in a spectrum containing a large number of bright lines superimposed upon the continuous spectrum of incandescent carbon (Fig. 175). In some cases, the bright lines are so numerous and so close together, that the spectrum may, for all practical purposes, be considered continuous.

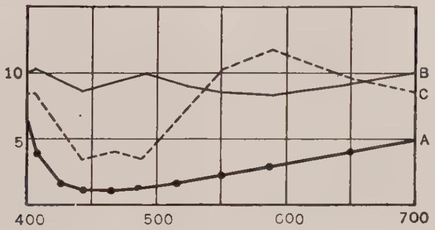

Fig. 175. Spectral Energy Curves: (A) Carbon, (B) White Flame, (C) Panchromatic Arc.

The arc lamps supplied for general photography are usually designed to operate at from 25 to 60 amperes, although much larger types are in use in motion picture production. The high intensity and sun arcs employed in the motion picture industry are also much more efficient than those in general use in portrait and commercial photography.

Lighting Equipment

Equipment for Incandescent Tungsten Lamps.—With the general adoption of panchromatic materials for both portrait and commercial photography, the incandescent tungsten lamp has become the most widely used form of artificial light. This is due to the fact that the incandescent lamp forms a clean, convenient, reliable source of light, while the spectral distribution of the light is well adapted to the requirements of contemporary panchromatic materials.

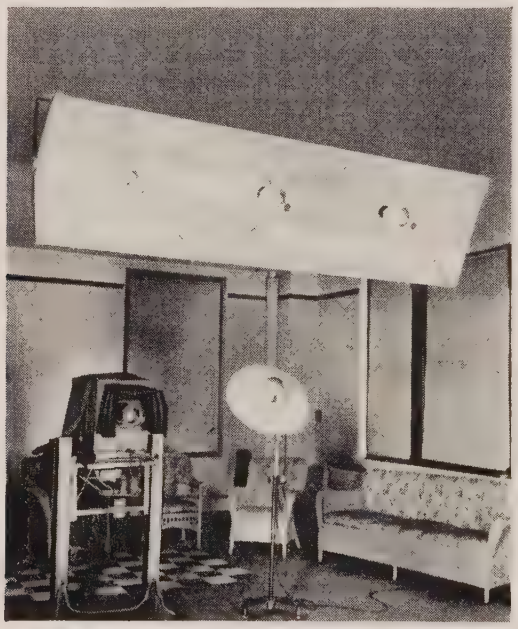

Fig. 176. Overhead Indirect Floodlighting Unit for Portrait Photography. (Johnson Ventlite Company.)

An indirect, overhead lighting unit for general studio illumination is shown in Fig. 176. This consists of a number of trough-like, aluminum reflectors attached to the ceiling. The 1000 watt tungsten lamps are covered with a deflector, which intercepts the direct rays, returning them to the main reflector where they are re-reflected resulting in a broad, highly diffused source of illumination.

A typical floodlight, or modeling light, designed more particularly for portrait photography is shown in Fig. 177. The 30 inch reflector of aluminum is adjustable to any angle and is mounted on a stand which provides a range in elevation from 3 to 9 feet. A deflector, placed directly in front of the 1000 or 2000 watt lamp, cuts off all direct light and returns it to the main reflector, thus producing a soft, well diffused source of illumination.

In general commercial and illustrative photography, floodlighting units of the type shown in Fig. 178 equipped with Fresnell lenses are widely used. The Fresnel lens, like the ordinary condensing lens, concentrates the light into a relatively narrow beam, but has the advantage of producing diffused rather than direct illumination.

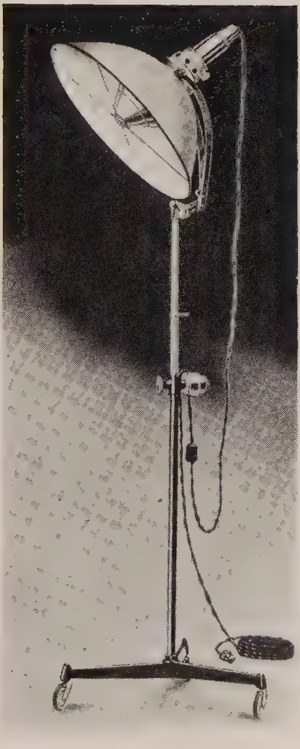

FIG. 177. Modelling Light Unit for Portrait Photography. (Johnson Ventlite Company.)

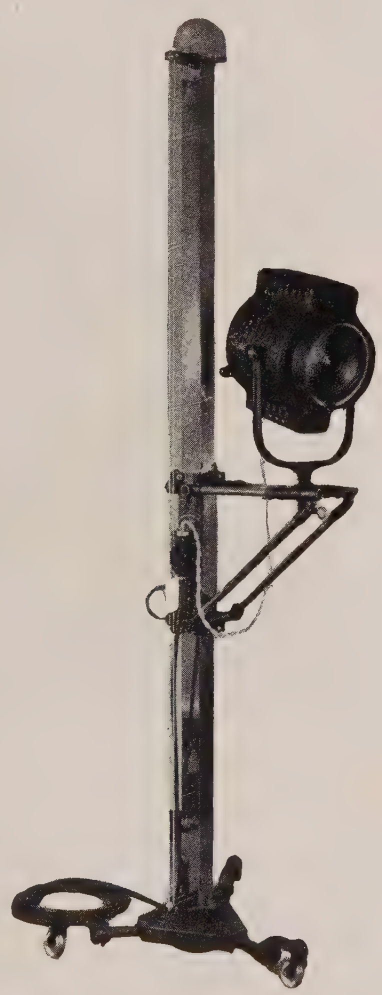

FIG. 178. Concentrating Floodlight Unit for Commercial and Illustrative Photography. (J. G. Saltzman Company.)

The spotlight projects a concentrated beam of light and is used to produce sharply defined highlights and shadows. Spotlights of the types illustrated in Fig. 179 employ a concentrated filament tungsten lamp behind a Fresnel lens or a condensing lens with a spherical mirror behind the lamp to concentrate the light on the condensing lens.

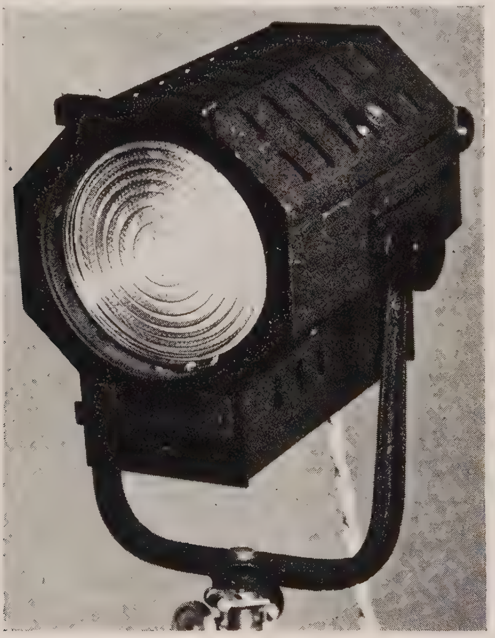

Fig. 179. Typical Spotlighting Unit. (J. G. Saltzman Company.)

Portable Equipment.—Compactness and portability are among the major requirements of lighting equipment for use away from the studio. Because of its greater carrying power, i.e., candle-power in a given direction, lighter weight and greater compactness, tungsten sources are preferred over all others for portable equipment. An example of tungsten lighting equipment for commercial photography away from the studio is shown in Fig. 180.

The reflectors are from 16 to 20 inches in diameter and are designed for use with either incandescent tungsten or photoflash lamps. These reflectors are given various shapes to adapt them to different lighting requirements. A highly polished parabola is supplied for use where it is necessary to project a comparatively narrow beam of light for some distance; an etched parabola for use at shorter distances, and two others spreading the light over angles of 45° and 60° respectively. The reflectors are supported on light weight folding stands, or suspended from the wall and nest together for convenience in carrying.

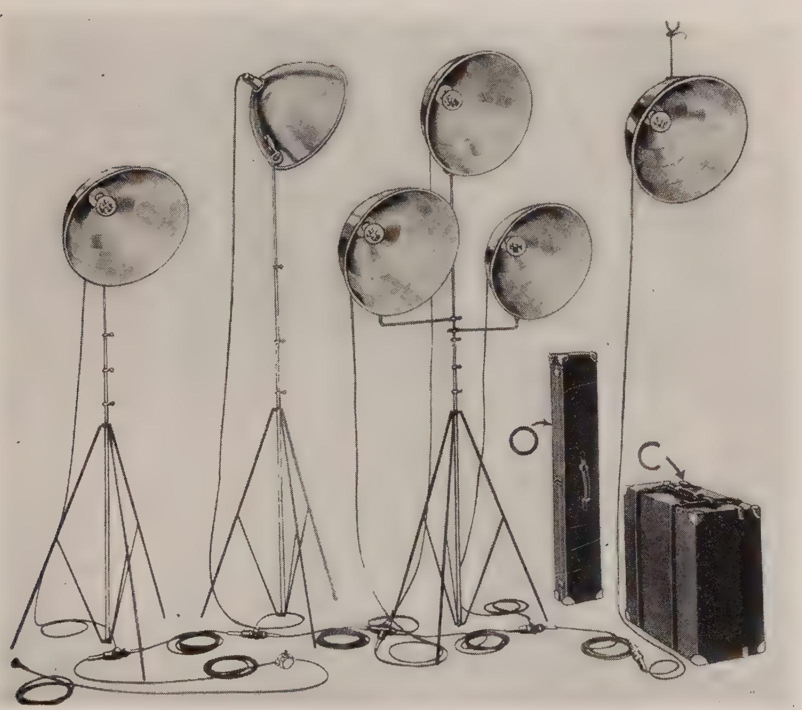

Fig. 180. Portable Lighting Equipment for Incandescent Lamps. (Johnson Ventlite Company.)

Arc Lighting Equipment.—A typical floodlighting unit employing a twin arc is shown in Fig. 181. The twin arc is generally preferred over the single since, with practically the same current consumption, the light intensity is nearly twice as great. An electrical relay mechanism controls the positions of the carbons so that the lamp requires no attention except when it is necessary to change the carbons. Automatic operation also results in a light source, which is more nearly constant in intensity. For floodlighting, the arcs are invariably enclosed in a box-like cabinet and in some cases, deflectors are provided to cover the arc so that only the light reflected from the sides of the cabinet is used.

The arc, being essentially a point source of light, is well adapted to spotlighting requirements. Spotlights employing an arc source do not, in general, differ essentially in design from those already described.

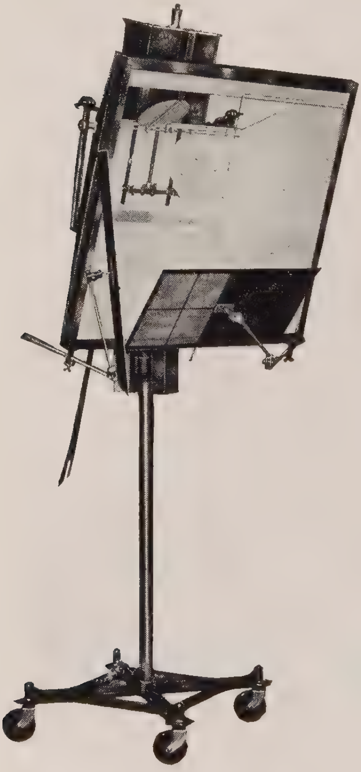

Fig. 181. Typical Arc Lamp for Portrait and Commercial Photography. (Photogenic Machine Company.)

Equipment for Fluorescent Lamps.—Fluorescent lamps, being an extended, highly diffuse source of light, have been used chiefly, up to the present time, in portraiture. A typical unit (Fig. 182) consists of a number of lamps, each with a trough-like reflector in a frame mounted on a stand, which enables the lighting unit to be raised or lowered as required. Similar lighting units are available for permanent installation on the studio walls, and small units with collapsible stands are available for home portrait work.

Care of Lighting Equipment.—Lamps or reflectors should be kept clean. Even in a comparatively clean district there is enough dust, smoke and soot in the air to justify regular cleaning of the lighting equipment once a month. In the downtown sections of a busy industrial city, or in close proximity to smoke and dust producing plants, more frequent attention is required. Clean lamps and reflectors with soap and water or a soft cleaning powder. Light diffusing materials, such as tracing cloth, china silk, and buckram, should be renewed every six months.

To obtain maximum efficiency from the light, the walls of the studio should be painted white, light ivory, or light gray. If the walls are dark, little light is reflected and practically all of the illumination comes directly from the lighting units; if the walls and ceiling are light, the light reflected provides illumination for the shadows and reduces the exposure.

Incandescent lamps should be burned at their stated voltage. If the voltage is too high, the lamps burn brightly but their life is unduly shortened. If the voltage is too low, the light output is greatly reduced and the actinic intensity of the light is reduced even more. Therefore, it pays to make certain that the rated voltage of the lamp corresponds with the actual voltage at which they are used.

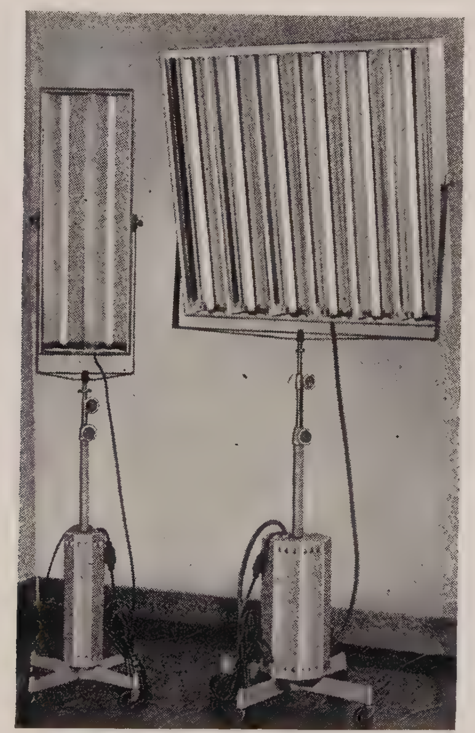

FIG. 182. Lighting Unit Employing Fluorescent Lamps.
(Johnson Ventlite Company.)

It is distinct economy to use, in each lighting unit, only the particular size and type of lamp for which the unit is designed. This is especially important in the case of spotlights and focusing reflector floodlights, both of which depend for efficient illumination upon the light source being in the proper position with respect to the optical system.

All electrical wiring, cords, switches, connections, etc. should be checked periodically and repaired or replaced at first sign of disorder to prevent possible damage to equipment, injury to operators, or fire danger.

Reflecting and Diffusing Mediums.—Reflectors increase the effective candle power of a light source by directing it towards the area to be illuminated. The reflector should, so far as possible, confine the light to the area to be illuminated; reflectors which spread the light over a larger area are wasteful of light. Specular surfaces form the most efficient reflectors, but are more costly to produce, and the surface is not as permanent or as resistant to wear. In addition, difficulty is frequently experienced in obtaining uniform illumination, owing to the imaging of the light source. Matt or semi-matt surfaces, which reflect diffused light, are preferable for most purposes.

The efficiency of a number of the materials used in the construction of reflectors for photographic lighting equipment is shown in the following table:[8]

Surface	*Character of Reflected Light*	*Per Cent Reflectance*
Silver plate	Specular	85–90
Glass mirror	Specular	80–90
Aluminum foil	Specular	85
Aluminum, Alzak	Specular	75–85
Aluminum, polished	Diffuse	70–80
Aluminum, oxidized	Specular	60–70
Aluminum, etched	Diffuse	70–85
Chromium	Specular	60–65
Chromium, satin	Diffuse	50–55
Stainless steel	Specular	55–65
Stainless steel, satin	Diffuse	50–55
Porcelain enamel, white	Diffuse	60–80

The effect of the reflecting surface on the spectral energy distribution of the reflected light is manifestly of importance in color photography, but no data appears to be available on this point.

Light Diffusing Materials.—Light diffusing material should diffuse or spread the light with as little absorption as possible. In the ideal case, the entire surface of the diffusing material should be uniformly illuminated and should appear equally bright when viewed from various directions. Such uniformity is extremely difficult of attainment, but the translucent materials at present available, when used in conjunction with properly designed reflecting equipment or several lamps correctly spaced, give a sufficient uniformity to meet photographic lighting requirements. Data on the more common types of translucent materials are given in the following table:

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[8] Compiled from data supplied by Nela Park Engineering Department, General Electric Company.

Materials	*Per Cent Light Transmitted*	*Diffusing Properties*
Tracing Cloth	60–70	Good
China Silk	60–70	Fair
Acid-Etched or Ground Glass	85–90	Good
Enamel-Coated Glass	20–30	Excellent
Rippled Glass	80–90	Fair

Flash Lamps.—In the latter part of 1930 the General Electric Company announced the first Photoflash lamp to appear on the American market. This lamp contained about 65 mg. of thin aluminum foil which was ignited by passing an electric current through a filament covered with a chemical primer. The bulb was filled with oxygen to a pressure of 170 mm. of mercury. This lamp gave a flash of relatively short duration (about 1/50 sec.) and of sufficient intensity to properly expose a subject under average indoor conditions.

Immediate acceptance of this lamp was inevitable since it abolished the fire hazard ever present with the open firing of magnesium powder and introduced a controlled light source thereby eliminating one of the variables of indoor picture taking. Amateurs used the lamp by the so-called " open flash " technique; i.e., they opened the shutter on " time," flashed the lamp to make the exposure, then closed the shutter. By this method satisfactory pictures could be taken of stationary or slow moving subjects simply by allowing the duration of flash of the lamp to control the exposure interval. In the early thirties many devices, known as synchronizers or flash guns, were introduced to synchronize the opening of between-the-lens shutters with the peak intensity of the flash in an effort to make possible flash photography at the higher shutter speeds. At the same time the lamp manufacturers attempted to standardize the time characteristics of their flash lamps so that the light emitted would reach maximum brilliance in 20 milliseconds [9] after the primer filament had been energized.

The duration above half peak intensity for the early foil-filled lamps was approximately 1/120 sec. This short duration made it rather difficult to synchronize the camera shutter at the higher shutter speeds, so that it would be open during this relatively short interval. To overcome this condition, the foil filling was replaced with a wire filling which burned at peak brilliance for a longer interval, thereby producing a lamp with a duration above half peak intensity of about 1/60 sec. Both leaf foil, shredded foil and wire-filled lamps are available today. The foil-filled lamp usually reaches a higher peak intensity than a wire-filled lamp of corresponding bulb size, while the wire-filled lamp gives a flash of somewhat lower peak intensity but of longer duration.

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[9] A millisecond is 1/1000 sec.; therefore 20 m.s. = 1/50 sec.

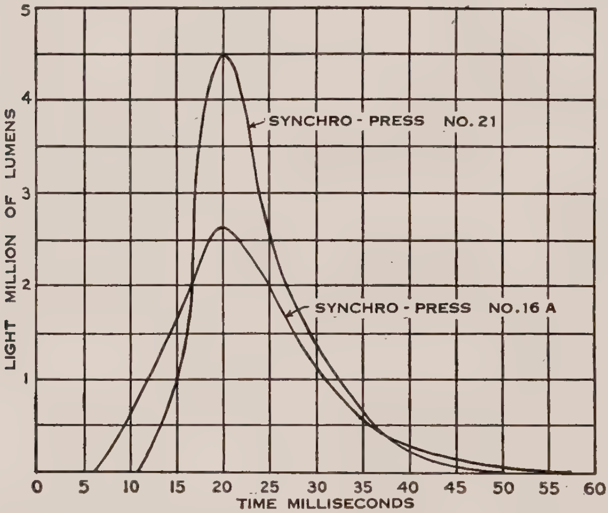

Fig. 183. Time-Light Curve of Nos. 16 A and 21 Flash Lamps.

Fig. 183 gives comparative time-light curves for the No. 16A Photoflash lamp, which is wire filled,[10] and the No. 21 lamp which is foil-filled. The following characteristics should be noted:

Lamp	No. 16A	No. 21
Filling	Shredded foil	Leaf foil
Peak Intensity, lumens	2,600,000	4,500,000
Duration of Flash above half peak intensity, m.s.	9	14
Time to Peak Intensity	20	20

A third type of flash lamp is available which permits synchronization with focal plane shutters. This is a wire filled lamp having a still lower peak intensity but with a very prolonged flash. Fig. 184 shows the time-light trace for the No. 6 and No. 31 focal-plane lamps. This long flash is needed so that light of constant intensity will be incident upon the subject throughout interval required for the focal-plane shutter slit to traverse the film. The No. 6 lamp is intended for use only with focal-plane cameras of the miniature type.

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[10] The wire filling in Mazda Photoflash lamps is referred to as shredded foil since the filling is made by shredding foil into thin wire-like strips.

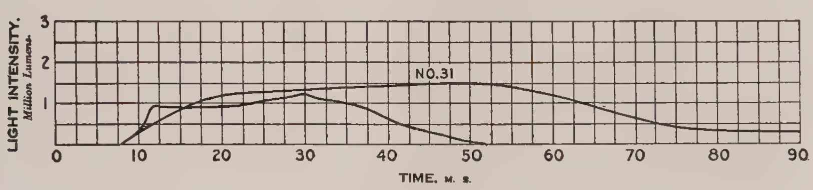

Fig. 184. Time-Light Curves for the Nos. 6 and 31 Flash Lamps for Synchronization with Focal Plane Shutters.

Flash Lamp Characteristics.—The following characteristics of a flash lamp should be known to describe fully its photographic usefulness as a light source:

1. Spectral quality of the radiation.
2. Total quantity of light emitted, *lumen-seconds.*
3. Maximum intensity of the radiation, *lumens.*
4. Time from application of the filament current to the *start* of the flash, m.s.
5. Time from application of the filament current to the *peak intensity* of the flash, sec.
6. Total *duration* of the flash above a specified minimum intensity, sec.

The time characteristics (Items 4, 5, and 6 above) can be readily determined by passing light from the lamp through a slit onto a sheet of film which is moved past a slit with a known velocity. A study of the variation in density of the resulting photographic trace gives a measure of the "photographic effectiveness" of the radiation directly as a function of time. A spark discharge flashed through the slit at the instant the filament circuit is closed records the zero point from which to make time measurements. Fig. 185 shows a density-time trace for a No. 5 Photoflash lamp which was obtained by exposing a 4 × 5 inch sheet of film in the G. E. Synchrograph shown in Fig. 186. This instrument consists of a rotatable drum in which is cut a longitudinal slit. Surrounding the drum is a light tight chamber which holds the film in a cylindrical shape of slightly greater radius than that of the drum. Light from the flash lamp enters the hole at one end of the synchrograph where it is spread by a conical mirror into a disc of light orthogonal to the axis of the drum. By rotating the drum at a known r.p.m., light from the lamp passes through the slit onto the film to expose the density trace of the lamp. Light from a momentary spark discharge which is flashed simultaneously with the closing of the lamp filament circuit enters the other end of the synchrograph, is deflected by a second conical mirror, and passes through the drum slit to establish the zero reference line shown in Fig. 185.

Intensity measurements for flash lamps can easily be obtained by allowing the light from the lamp to fall upon the surface of a photo tube which is connected through a suitable amplifier to a string oscillograph. Time-light curves obtained in this manner are shown in Fig. 187. The wavy character of the time-light curves is caused by superimposition of the trace of a 1000-cycle tuning fork onto the time-light curves. This procedure gives a convenient

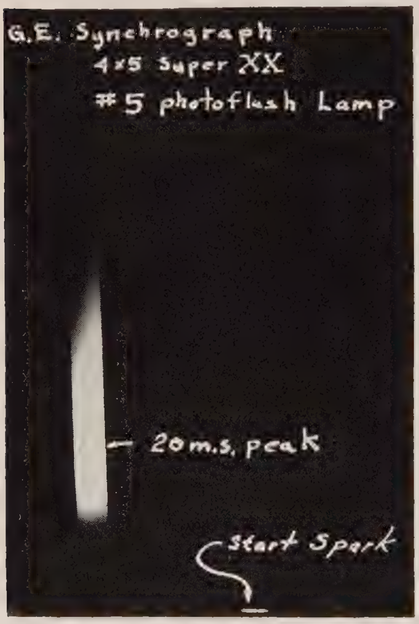

Fig. 185. Synchrograph Trace of No. 5 Lamp.

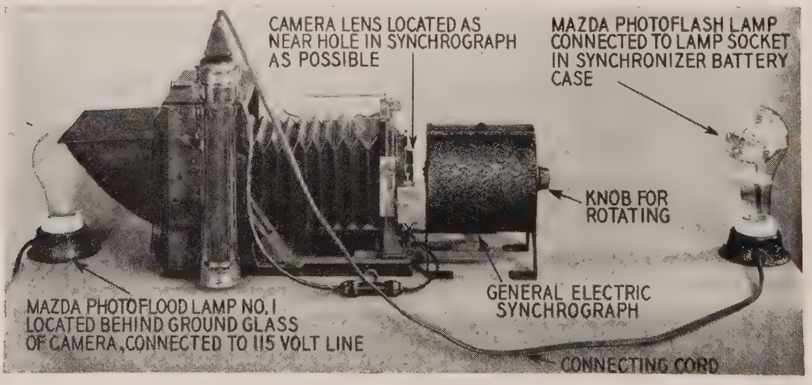
CAMERA LENS LOCATED AS NEAR HOLE IN SYNCHROGRAPH AS POSSIBLE
MAZDA PHOTOFLASH LAMP CONNECTED TO LAMP SOCKET IN SYNCHRONIZER BATTERY CASE
KNOB FOR ROTATING
GENERAL ELECTRIC SYNCHROGRAPH
MAZDA PHOTOFLOOD LAMP NO. I LOCATED BEHIND GROUND GLASS OF CAMERA, CONNECTED TO 115 VOLT LINE
CONNECTING CORD

Fig. 186. General Electric Synchrograph.

method of measuring time along the curve, since the time between each peak of the tuning fork disturbance is exactly one millisecond. Curve 5 (Fig. 187) is for a No. 11 lamp operated with two 1½ volt D cells having a short circuit current of 5 amps. It will be noted

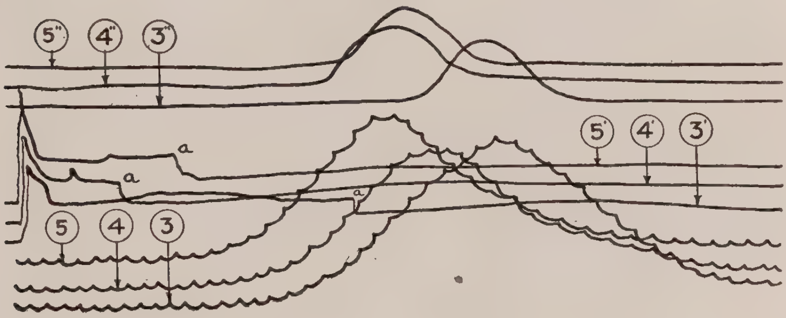

FIG. 187. Oscillograph Tracings of a No. 11 Flash Lamp.

that under these conditions the lamp reaches peak intensity in 20 milliseconds after the current is applied. Curves 4 and 3 are for No. 11 lamps when fired with two 1½ volt D cells with short circuit currents of 4 and 3 amps respectively. It is apparent that the weaker batteries slow down the lamp materially. For these tests the lamps were flashed in a Kodak Senior Synchronizer (see Page 196) which has an electromagnet of 2.4 ohms resistance connected in parallel with the lamp. The ordinate values for these time-light curves are found by calibrating the oscillographic equipment against a standard incandescent lamp of known brightness and color temperature.

Curves 5′, 4′, and 3′ in Fig. 187 show the current through the lamp filament and the time to filament burn out for each case. It will be observed that the filament current rises sharply at the instant the circuit is closed but drops to a steady value within one to two milliseconds. The sharp break in the current trace at point A shows where the filament burned out. It is apparent that the time to filament burn-out is greatly prolonged by using weak batteries.

Spectral Distribution of Flash Light.—The spectral character of a light source having a continuous spectrum may be specified conveniently by giving the color temperature of the source. The color temperature is defined as the temperature to which a black body must be raised so that the light it emits has the same integral color as that

TABLE 1. CHARACTERISTICS OF MAZDA PHOTOFLASH LAMPS *

Lamp No.	*SM++*	*5*	*5B*	*11*	*16A*	*21+*	*21B+*	*22*	*50*	*75*	*6*	*31*
Bulb	B11	B11	B11	A15	A17	A19	A19	A19	A21	PS35	B11	A21
Bulb volume (cc)	25	25	25	70	95	140	140	140	190	800	25	190
Total light output in lum.-sec.	5,000	18,000	6,000	30,000	43,000	50,000	17,000	65,000	110,000	160,000	18,000	75,000
Max flux in million lumens	0.8	1.2	0.4	2.4	2.6	4.5	1.6	4.0	5.5	9.5	0.5	1.5
Time in sec. from close of circuit to:												
Peak of flash †	0.005	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.030	0.035–0.040		
One-half max. int.†	0.0035	0.015	0.015		0.014	0.016			0.023		0.012	0.015
Filament burn-out†	0.0015	0.0025	0.0025	0.0020	0.0025	0.0015	0.0015	0.0015	0.0015		0.0015	0.0015
Effective duration of flash (sec.) ‡	0.0035	0.012		0.015	0.015	0.010			0.013	0.010	0.030	0.055
Color temp, °K.	3300	3800	6300	3800	3800	3600	6300	3800	3800	3450	3800	3800

* Measurements made in Lamp Development Laboratory, Nela Park, Cleveland, Ohio.

† Lamps flashed on 3 Type D cells.

‡ Approximate duration of light intensity above a half million lumens.

+ No. 21 and No. 21B lamps leaf foil-filled.

++ SM lamp has no filling; all others shredded foil-filled.

of the source being considered. Thus, for example, if a flash lamp has a color temperature of 3600° K, it means that the light from the lamp has the same integral color as that from a black body operated at a temperature of 3600° K. The color temperature of a flash lamp is usually specified for only that light having an intensity above a half million lumens to avoid the light emitted at the beginning and end of the flash where the temperature of the aluminum filling is rising or falling.

The table on Page 190 gives the operating characteristics of G. E. Photoflash Lamps, including the color temperature for each lamp. It will be noted that all of these lamps operate at a color temperature lying between 3450° K. and 3800° K. except the No. 5B and No. 21B lamps which are specially coated with a blue lacquer to raise the color temperature to 6300° K. so that it will be a suitable source for use with Kodachrome film balanced for daylight use.

Since both orthochromatic and panchromatic emulsions can be exposed by either daylight (5400° K. upwards) Photoflood light (3400° K.), or regular tungsten lamps (2850° K.), it is apparent that these emulsions can be exposed properly with any Photoflash source which has a color temperature lying between these limits.

The following table will be found helpful in selecting the proper filter to use when exposing Kodachrome Films by Photoflash light:

	Kodachrome Type A	*Professional Kodachrome Type B*
Leaf Foil Filled Lamps	CC-13	CC-15
Wire or Shredded Foil Filled Lamps	CC-15	2 A

The Photoflash lamps listed in this table (except the No. 5B and No. 21B) can be used in this manner with Kodachrome Films balanced for tungsten illumination.

Kodachrome film (daylight type) requires a much bluer light than that emitted by regular flash lamps since this film is balanced to give proper color rendition by daylight (5400° K.). The No. 21B and No. 5B lamps are coated with a blue lacquer which was developed by the Kodak Research Laboratory and has such a transmission that the light from the bulb is of the proper color temperature to supplement daylight in taking pictures with Kodachrome film balanced for daylight. Fig. 188 compares the spectral transmission of the blue lacquer with that of an ideal filter that would transform light from a No. 21 or 5 lamp to a color temperature of 6500° K., which is within the range of color temperature of the light for which this type of Kodachrome film is balanced.

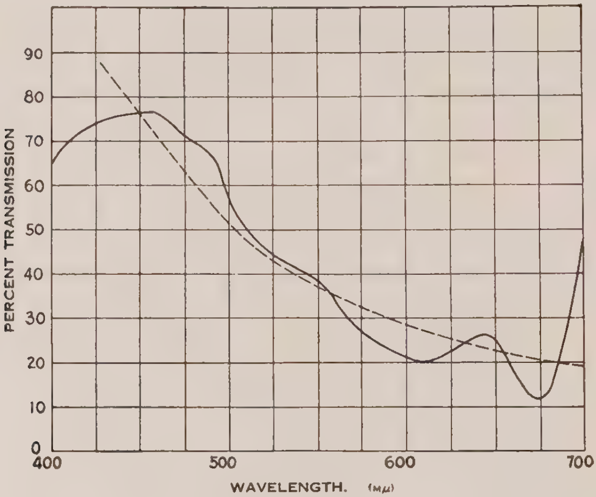

Fig. 188. Spectral Transmission of Lacquer Used on Nos. 5B and 21B Lamps.

Synchronization.—Manually set camera shutters, such as the Supermatic, Kodamatic, Diomatic and Compur, require about 5 milliseconds for the shutter blades to reach the full open position; i.e., 5 milliseconds elapses between the instant when the shutter is tripped and the shutter blades open fully. The duration of the interval during which the shutter remains open depends upon the shutter speed. The following table gives average values for the duration of full shutter opening for several shutter speeds. Fig. 189 shows a graphical record of these shutter characteristics together with a trace of the time-intensity curve of a typical flash lamp which was energized at the

Shutter Speed	*Time for Shutter Blades to Reach Full Opening, m.s.*	*Duration of Full Opening, m.s.*	*Total Elapsed Time between Tripping Shutter and Closing of Blades, m.s.*
1/400	5	2.5	8.5
1/200	5	5	11
1/100	5	10	16
1/50	5	20	26

same instant that the shutter was tripped. From this record it may be seen that no light from the lamp passed the shutter at either the 1/400 or 1/200 speeds, and that an insufficient percent of the total light reached the film at the 1/100 speed. Hence we may conclude that simultaneous flashing of the lamp and tripping the shutter would give satisfactory results only for those shutter speeds slower than 1/100 second.

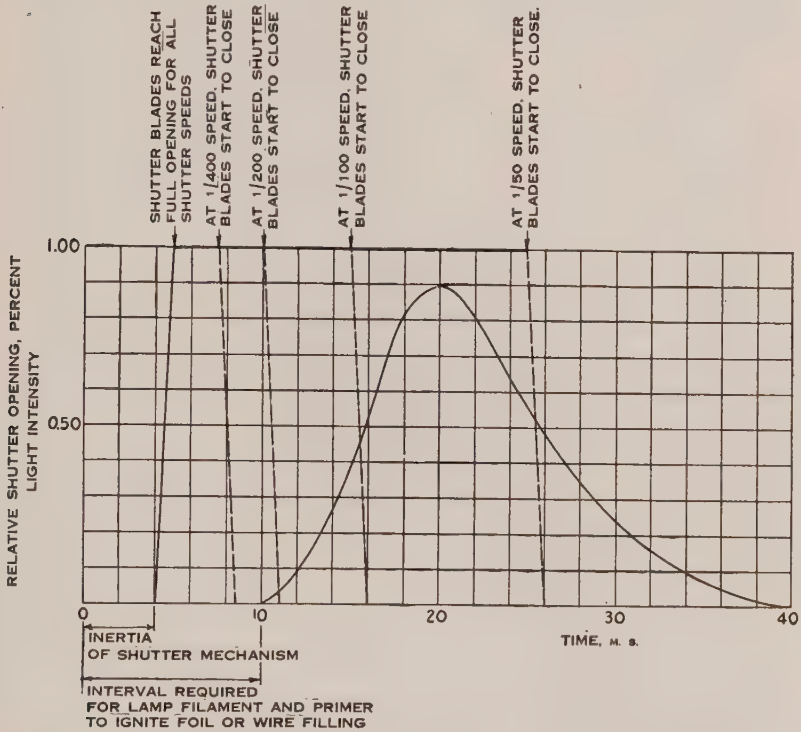

Fig. 189. Shutter and Lamp Curves Showing Timing when Lamp is Flashed at Instant of Tripping Shutter.

To overcome this difficulty various synchronizing devices have been made which delay tripping the shutter until 12 to 15 milliseconds after the lamp circuit is closed. In this manner the shutter action is retarded sufficiently to allow the lamp to almost reach peak intensity before the shutter blades reach the full open position. A graphical representation of a properly synchronized shutter is shown in Fig. 190. It will be seen that when the shutter action is sufficiently retarded it is possible to take pictures at any desired shutter speed since ample light is passed by the shutter at all speeds.

Self acting shutters, such as the Kodex and Dakon, require about 13 to 15 milliseconds to reach the full open position. For this reason, a delay type synchronizer mechanism is not required for these shutters since flashing the lamp at the instant the shutter is tripped results in the shutter blades being fully open during the peak intensity of the lamp. Self acting shutters in general do not have shutter speeds greater than 1/100 sec.; therefore the blades remain fully open for a sufficient duration to pass ample light from the flash to the film.

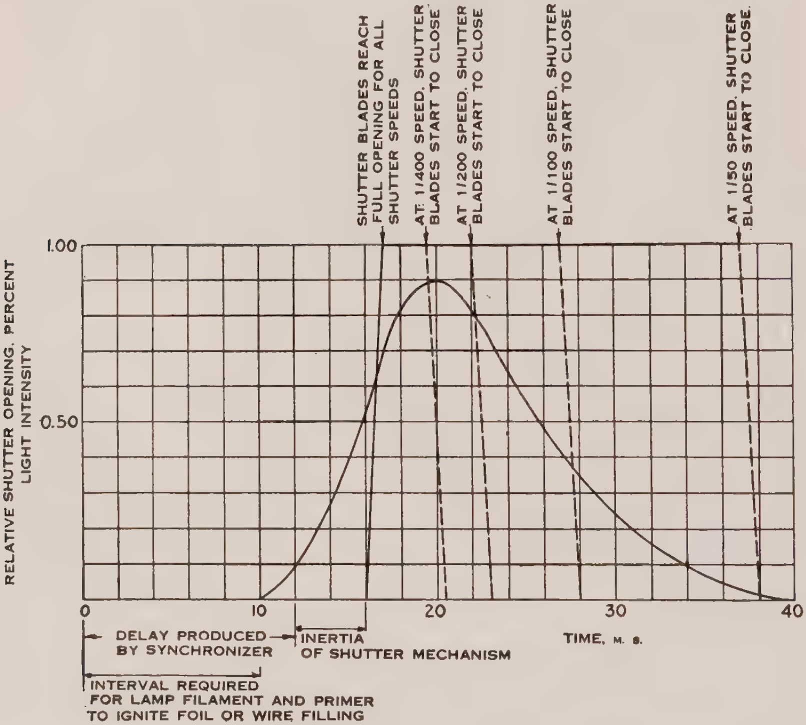

Fig. 190. Shutter and Lamp Curves for Properly Synchronized Shutter.

Synchronizers.—Devices for synchronizing the shutter action with the flash of the lamp may be divided into two types: (1) mechanical synchronizers and (2) electromagnetic synchronizers.

The Kalart Micromatic Speed Flash, shown in Fig. 191, is representative of one of the better mechanical synchronizers in popular use today.

The synchronizing device, which attaches directly to the camera shutter, is electrically connected to a suitable battery case which accepts the flash lamp and holds a reflector to direct light from the lamp toward the subject. In operation, a disc within the synchronizer housing is manually rotated against the action of a helical spring until a small pawl engages the disc, holding it in the "cocked" position. When pressure is applied to the cable release, the pawl is depressed and a flat silver spring makes contact against a screw which is connected to one of the lead-in wires to the battery case. The helical driving spring is always in contact with the wall of the synchronizer housing to which the other lead-in wire is grounded. Thus, when the cable release is pressed, the action of the pawl causes the electrical circuit to be completed thus firing the lamp.

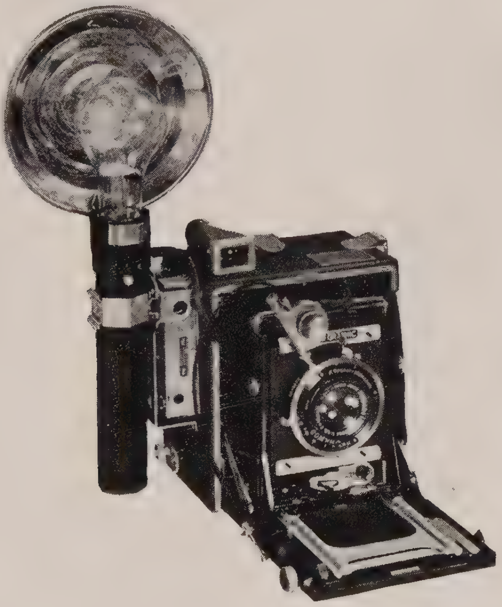

FIG. 191. Kalart Micromatic Speed Flash Synchronizer.

The disc then starts in motion, actuated by the tension of the helical spring. After about 12 to 15 milliseconds of rotation, the disc reaches a position where it allows a small spring-driven plunger to enter the shutter with just sufficient force to trip the shutter. From this explanation it is seen that the electrical circuit is closed when the pawl is pressed by the cable release sufficiently to free the spring driven disc which, 12 to 15 milliseconds later, releases the plunger to trip the shutter.

With mechanical synchronizers the electrical energy supplied by the battery is used only to raise the filament of the flash bulb to incandescence. The circuit is automatically broken when filament burnout occurs. Because of this, each flash lamp fired drains but a negligible amount of energy from the batteries, and consequently long battery life results. Considerable care must be exercised in the design and manufacture of the moving contacts employed in mechanical synchronizers, since high contact resistance or vibratory erratic contact will seriously delay the time to peak intensity of the lamp. Some mechanical synchronizers are so made that the tripper mechanism is influenced by the rapidity with which the operator presses the cable release. Devices of this nature cannot be free from the subjective effect of the operator, and therefore are not as reliable as a device which completes its cycle of operations in a predetermined manner.

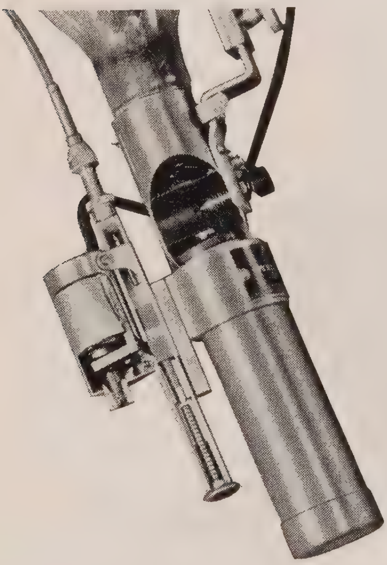

Fig. 192. Cut-away Model of Kodak Senior Synchronizer, Speedgun Model E.

Fig. 192 shows a cut-away view of the Kodak Senior Synchronizer, Speedgun Model E. This is a typical electromagnetic synchronizer which operates the camera shutter through a cable release. In operation a spring loaded plunger is manually moved to the " cocked " position (as shown in Fig. 192) where it is held by a small pawl. When the synchronizer switch is pressed both the lamp and electromagnet circuits, which are connected in parallel, are closed simultaneously. The air gap in the magnetic circuit of the solenoid is adjusted to allow about 12 milliseconds to elapse before sufficient flux density is built

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Morgan—Synchroflash Photography. Morgan & Lester, Publishers, New York.

up to withdraw the pawl and thereby release the plunger. When the plunger is released it travels upward under the action of the spring striking the end of the cable release which in turn trips the shutter.

By proper coil design, i.e., correct balance of resistance, ampere-turns, and magnetic reluctance, it is possible to have both the lamp and shutter remain in matched synchronization throughout a wide range of battery amperage. The curves shown in Fig. 190, Page 194, illustrate this condition for new batteries having a short circuit current of 5 amperes to practically exhausted batteries having a short circuit current of but 3 amperes. These curves show that while the lag of the lamp is increased as the batteries age, the action of the coil is slowed up so that the shutter opening is also delayed by a corresponding amount.

If the coil of a magnetic synchronizer has a resistance much below 2 ohms it will drain too much current from the batteries and consequently slow down the flashing of the lamp. Electromagnetic synchronizers of this type are very sensitive to changes in battery amperage and are quickly thrown into malsynchronization as the batteries age.

Multiple Flash.—Frequently photographers wish to synchronize more than one flash bulb with the camera shutter in order to obtain better subject modeling than is possible with a single light source. These extension flash lamp sources are wired in parallel to the lamp socket on the synchronizer battery case. The added resistance of this wiring and the resistance of the contacts should not be greater than 0.5 ohms; otherwise the time lag of the lamps will be increased more than is allowable for synchronization. The effect of circuit resistance upon the timing of the lamps is shown in the table below.

EFFECT OF RESISTANCE ON TIMING OF PHOTOFLASH LAMPS FLASHED ON 3 VOLTS (TWO TYPE D DRY CELLS)

Length of No. 18 Stranded Wire Two Conductor Lamp Cord	*Time from Contact to Peak Intensity, m.s.*		
	No. 21 Lamp	*No. 16A Lamp*	*No. 5 Lamp*
0	20	20	20
25 ft.	22	21	22
50 ft.	35	22	23

Battery Resistance.—Since the internal resistance of the batteries is in series with the flash lamp at firing it is important to use batteries which have a fairly low and stable internal resistance. The small penlite cells have an internal resistance two to three times as great as that of D cells. Since the internal resistance of all batteries increases with age it is good practice to replace batteries every month, especially the smaller. The table below gives a comparison of the time to peak intensity of lamps flashed on penlite and type D cells for various voltages. It will be observed that satisfactory performance is obtained with little change in peak lag for voltages between 3 and 18 volts.

EFFECT OF VOLTAGE ON TIMING OF PHOTOFLASH LAMPS

Voltage	*Cell Type*	*Time (m.s.) from Contact to Peak Intensity*	
		No. 21 Lamp	*No. 16A Lamp*
1.5	Penlite	—	25
1.5	Type D	35	22
3.0	Penlite	23	23
3.0	Type D	20	20
4.5	Type D	19	19
9.0	Type D	19	19
18.0	Type D	18	19
110.0	A.C.	15	—

Testing Accuracy of Synchronization.—The synchronizer should be tested from time to time for accuracy of synchronization. This can be done visually with sufficient precision by the following method: Secure a three-foot extension lamp cord having a bulb socket at one end and a male plug at the other. Screw a flash bulb into the socket and insert the plug into the bulb receptacle on the synchronizer battery case. Place the bulb behind the camera with the camera back open, having no film in the camera. Set the lens at maximum aperture and the shutter at the desired shutter speed. With the synchronizer and shutter cocked, fire the synchronizer at the same time looking directly into the lens. A brilliant flash of light will be seen through the shutter if the unit is synchronized properly.

More accurate tests can be made with the G. E. Synchrograph, Fig. 186. Using a 3 foot extension cord, place the flash bulb in front of the opening at one end of the Synchrograph. Arrange the camera so that its lens is in front of the opening at the other end of the Synchrograph. Place a lighted Photoflood lamp in back of the camera with the camera back open. Connect the extension flash lamp cord to the receptacle on the synchronizer battery case. With the Synchrograph loaded with a sheet of 4 × 5 in., slowly rotate the drum of the Synchrograph and fire the synchronizer,—having previously set the lens at maximum aperture and the shutter at the desired speed. Upon development of the Synchrograph film a record similar to that shown in Fig. 193 will be obtained if the synchronizer is in proper adjustment. This testing procedure gives an exact record of the time relation between the peak light and the shutter opening.

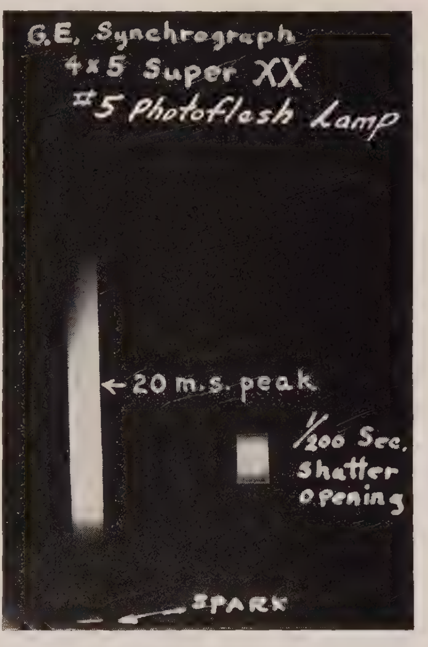


Fig. 193. Synchrograph Record of Properly Synchronized Shutter.

Reflectors.—Flash lamps are usually fired in a reflector which directs the light toward the subject. The light output values for the various Photoflash lamps given in Table I are for lamps flashed in the open without a reflector.

For the larger bulb sizes (11, 16A and 21) a properly designed portable hand-held reflector will increase the light available at the subject from 3 to 5 times that obtained with a bare lamp. Greater efficiency than this can only be obtained by flashing the lamps in studio type reflectors which are sufficiently large to collect and redistribute a higher percentage of the total radiation.

With the advent of the small No. 5 Photoflash lamp it became possible to design hand-held reflectors which give a 50° to 60° direct beam containing 5 to 9 times as much light as that emitted through this solid angle by the bare lamp. Thus because of the higher reflector efficiency made possible by the smaller bulb size, the No. 5 lamp has about the same photographic effect as the larger No. 11 lamp in a reflector of the same diameter. Recently focusing reflectors have been introduced for use with the No. 5 lamp which permit special spotlight effects at greater distances than the larger lamps.

The S. M. Photoflash Lamp.—In March 1941 the General Electric Company announced a new midget type Photoflash lamp called the

SM (Speed Midget) which has the same size as the No. 5 lamp but radically different characteristics. The SM lamp contains neither foil nor wire filling. A heavy coating of primer carried by the filament and lead-in wires burns in oxygen to produce the light emitted by the lamp.

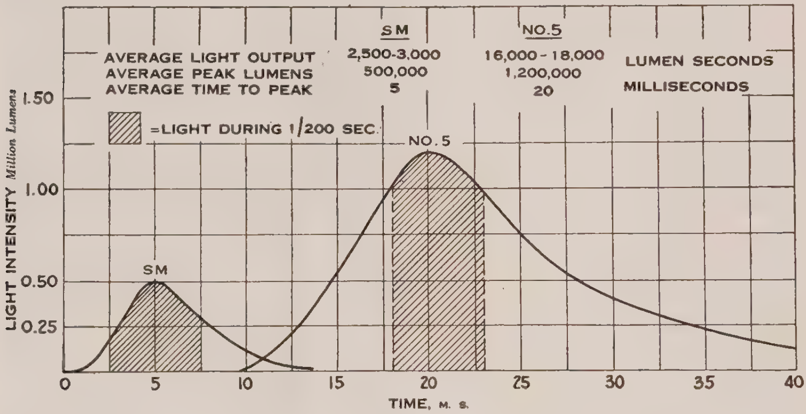


Fig. 194. Time-Light Curves for Nos. SM and 11 Lamps.

Combustion takes place so rapidly that the light reaches peak intensity in but 5 milliseconds after the filament is energized, rather than the 20 milliseconds delay required by foil and wire filled lamps. It will be recalled that manually set shutters such as the Supermatic and Compur shutters require but 5 milliseconds for the blades to reach the full open position. Therefore the synchronization of the SM lamps with these shutters may be easily obtained by firing both lamp and shutter at the same instant, thereby eliminating the necessity for any shutter delay mechanism.

The total duration above ½ intensity of the flash from an SM lamp is but 3.5 milliseconds (1/200 sec.); therefore for all shutter speeds of 1/200 and slower the flash of the lamp will control the exposure interval. The peak intensity of this lamp is about 800,000 lumens, which is sufficient for satisfactory exposures on Super XX film at 35 feet with an *f*/4.5 lens provided the lamp is flashed in a reflector having a relatively high efficiency. Fig. 194 gives a comparison between the time-light characteristics of the SM lamp and the No. 5 lamp.

Exposure Considerations.—To expose a photographic emulsion correctly by means of a synchronized Photoflash lamp source the following variables must be known and properly related:

1. Sensitivity of the film to the light emitted by the flash lamp.
2. Total quantity of light emitted by the lamp.
3. Efficiency of the lamp reflector.
4. Average reflection factor of the subject.
5. Percentage of total reflected light from the subject which is passed by the shutter.
6. *f*/number employed.
7. Lamp-to-subject distance.

It is common practice to publish exposure tables which specify the recommended *f*/number for a given lamp-to-subject distance, when using a particular film and lamp combination, at a given shutter speed. However, since exposure depends not only upon the lamp and film used, but also upon the reflection factor of the surroundings, these data should be adjusted for the actual conditions under which the pictures are being taken. This adjustment is more necessary when Kodachrome is being used, since the exposure is more critical for this film.

If a film is to be exposed properly by the light emitted from a given flash lamp, the *f*/number and lamp-to-subject distance must be so related that the quantity of light falling upon the emulsion surface is of sufficient magnitude to expose the film correctly. It is also important that this quantity of light be held at a constant value for all lamp-to-subject distances if uniform exposures are to be obtained.

It will be recalled that the quantity of light reaching the film varies inversely as the square of both the *f*/number and lamp-to-subject distance. This may be stated as follows:

$$E = k\left(\frac{1}{(f/\text{no.})^2}\cdot\frac{1}{d^2}\right), \tag{1}$$

where E = exposure received by the film,
k = a constant whose value depends upon the sensitivity of the film, the light output of the lamp, the average reflectivity of the subject, the shutter speed, and the efficiency of the reflector,
d = lamp-to-subject distance.

From Eq. 1, it will be seen that the product of the $(f/\text{no.})^2$ and (lamp-to-subject distance)^2 must be held constant if the exposure received by the film is to remain fixed, or

$$(f/\text{no.})^2 \cdot d^2 = K. \tag{2}$$

By extracting the square root of both sides of the above equation, we may write,

$$f/\text{no.} \cdot d = \sqrt{K} = G. \tag{3}$$

The constant G is often referred to as a Guide Exposure Number.

Both film and lamp manufacturers publish Guide Exposure Numbers which are determined experimentally by taking pictures under carefully controlled conditions at all shutter speeds and with each lamp and film combination. From the proper Guide Exposure Number, the correct f/number to use at any lamp-to-subject distance may be found by substituting in Eq. 3. For example, if the Guide Exposure Number for a No. 16A Photoflash Lamp at 1/100 second with Kodak Super-XX Film is 220; at 10 feet (lamp-to-subject distance) the proper f/number would be $\frac{220}{10} = f/22$; at 20 feet, the f/number would be $\frac{220}{20} = f/11$, etc.

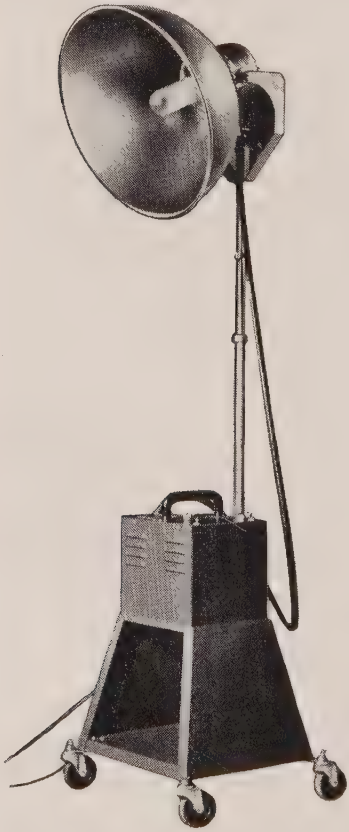
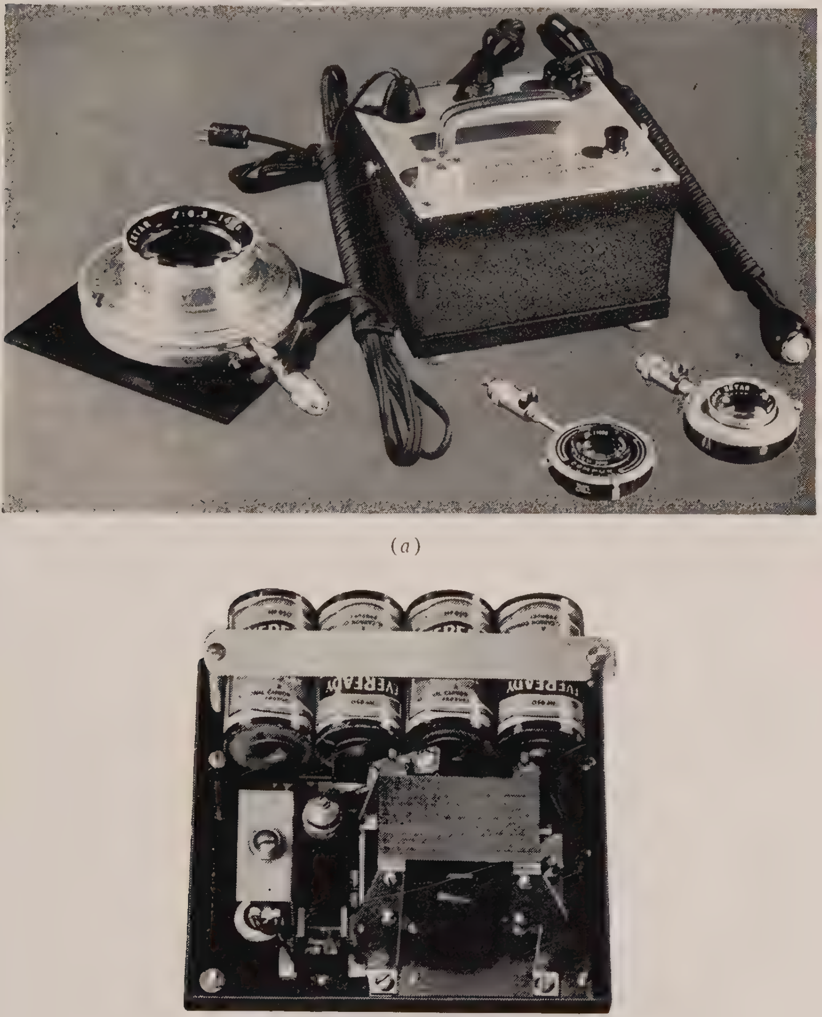


Fig. 195. Kodatron Speedlamp.

Kodatron Speedlamp.—In August, 1940, the Eastman Kodak Company announced an ultra-fast repeatable flash source which had been developed at the Massachusetts Institute of Technology by Messrs. Edgerton, Germeshausen, and Grier. This lamp, known as the Kodatron Speedlamp, produces a flash of very high actinic value and of extremely short duration. With but a single lamp, exposures can be made at f/16 at 20 feet with a flash duration reaching peak intensity in 1/30,000 second.

The Kodatron Speedlamp utilizes a gas-filled, electrically operated flash tube which provides an extremely high volume of soft light for photographic purposes. The Kodatron flash is produced by discharging a condenser through the flash tube. Ordinary 110-volt, 60-cycle current is led into the power unit of the lamp where a specially constructured transformer steps it up to 2000 volts. This current is then rectified and charges a condenser from which it is discharged through



(*a*)

(*b*)

Fig. 196. Kodatron Synchro-Timer.

the gas-filled tube. The flash is of high intensity but of short duration and not at all disturbing—in fact, one scarcely sees the flash. The Kodatron Speedlamp, Fig. 195, consists of a power unit mounted in a metal stand, an 18-inch reflector, and a flash tube on a telescoping steel support which can be raised to a height of 8 feet. The base is fitted with rubber-tired ball-bearing casters.

Since only a small fraction of a millisecond is required to complete the flash of the Kodatron Speedlamp it can be used effectively for stopping extremely fast motion. Pictures of ballet dancing, wrestling and boxing matches, and the like, result in critically sharp definition in all parts of the subject irrespective of the rapidity with which the action takes place. Speedlamp portraits possess a realism which can be achieved easily by posing the subject under room level illumination. When the desired pose is observed it is only necessary to flash the lamp to instantly record this pose on the film.

Under low illumination levels pictures can be taken using the open flash technique of opening the shutter, flashing the lamp and then closing the shutter. However, where the general room illumination is high enough to record a secondary image on the film it is necessary to synchronize the flash of the Speedlamp with the shutter, and use a high enough shutter speed to prevent sufficient secondary image forming light from reaching the film. In other words, the flash from the Speedlamp must produce the entire image on the film if the motion stopping ability of the flash is to be secured.

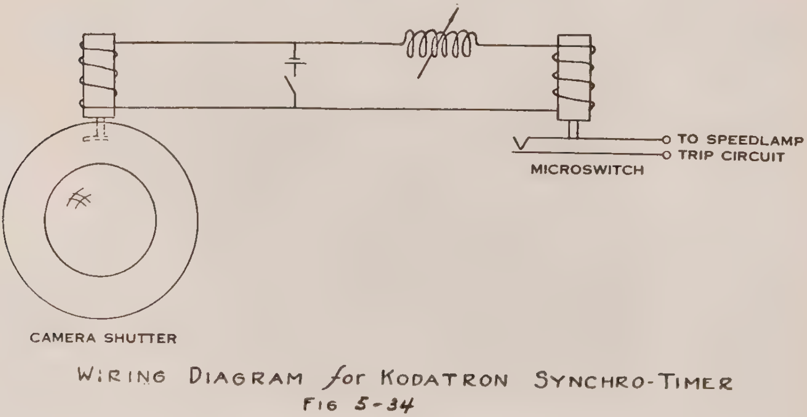


FIG. 197. Wiring Diagram for Kodatron Synchro-Timer.

The flash from the Speedlamp is completed in less than one millisecond after the trip circuit is closed. The time to full shutter opening for most manually set shutters is approximately 5 milliseconds. Therefore, for a device to synchronize the flash from this lamp with the action of the shutter it must perform the reverse function of a synchronizer intended for use with flash lamps; namely, it must delay the closing of the lamp circuit until the shutter has opened fully. The Kodatron Synchro-Timer, shown in Fig. 196, was designed to accomplish this. Fig. 197 shows the wiring diagram for this timer which consists of two matched solenoids connected in parallel across a suitable battery. One solenoid serves to trip the camera shutter while the other actuates a micro-switch which in turn closes the Speedlamp trip circuit. A variable inductance, wired in series with the micro-switch solenoid, delays its action until after the shutter solenoid has tripped the shutter. The length of this delay can be controlled by adjustment of the variable inductance so that the Speedlamp is flashed at the instant the shutter blades reach the full open position.

CHAPTER VI

PHOTOCHEMISTRY

Photochemistry.—The study of the chemical changes produced by radiation is known as photochemistry. The term radiation includes all forms of radiant energy as: visible light, ultra-violet, x-rays, gamma rays, infra-red, electric and cosmic rays. Chemical changes, or reactions, are caused by molecules or atoms that have become activated. According to the principles of chemical kinetics, molecules, or atoms, are activated when they absorb energy due to collisions with other molecules and atoms, or when they absorb radiant energy, such as light, from an external source. Only the radiation having the proper frequency and energy to be absorbed can effect a chemical change.

The types of radiation are differentiated from each other by differences in wave length. Wave lengths are commonly expressed in millimicrons, $m\mu$, or Angstrom Units (Å).

$$1\ m\mu = 1 \text{ millionth of } 1 \text{ millimeter},$$
$$1\ A = 1/10 \text{ millionth of } 1 \text{ mm.}$$

or

$$1\ m\mu = 10^{-6} \text{ mm.} = 10^{-7} \text{ cm.},$$
$$1\ \text{Å} = 10^{-8} \text{ cm.},$$
$$1 m\mu = 10\ \text{Å}.$$

Since the velocity of light is constant, 3×10^{10} cm. per second, the frequency of vibration can be calculated from

$$\lambda\nu = c,$$

$$\nu = \frac{c}{\lambda},$$

where c = velocity of light and λ (lambda) = the wave length in centimeters per second, and ν (nu) is the frequency of light.

Quanta.—While radiation is propagated in a form of wave motion, Planck showed, in 1901, that radiant energy is emitted, or absorbed discretely in small particles or units of energy called quanta. The quantum theory states that radiation is discontinuous and that certain restrictions apply when this energy is transferred to molecules or electrons. The energy of the quantum varies with the frequency of the radiation:

$$\epsilon = h\nu,$$

where ϵ (epsilon) is the energy of the quantum, h is Planck's constant equal to 6.547×10^{-27} erg. sec., and ν (nu) is the vibration frequency. From this it will be seen that as the wave length of the radiation decreases, the frequency becomes greater, and the energy of the quantum becomes larger.

QUANTUM ENERGY FOR DIFFERENT RADIATIONS

Radiation	*Wave length*	*Frequency*	*Quantum Energy*
X-ray..............	1 Å	3×10^{18}	1.96×10^{-8} ergs
Ultraviolet..........	1,000	3×10^{16}	1.96×10^{-11} "
Visible, violet........	4,000	7.5×10^{14}	4.91×10^{-12} "
Infra-red, short......	10,000	3.5×10^{14}	1.96×10^{-12} "

Einstein has shown that light quanta not only carry energy but have a mass which varies in proportion to the energy, according to the relativity equation:

$$m = \frac{h\nu}{c^2},$$

where c is the velocity of light.

The quantum theory has been particularly successful in explaining the photoelectric effect, black-body radiation, x-ray emission, and the discontinuous series of spectra.

The Photoelectric Effect.—In 1905 Einstein extended Planck's ideas and proposed that heat and light were composed of quanta. The quantum of light then became a corpuscle of light, now better known as the photon. By the use of this assumption, instead of the classical wave theory Einstein was able to overcome certain difficulties in explaining the photoelectric effect.

Einstein predicted that when the surface of the metal is exposed to light, the energy of the quantum is used to expel electrons from atoms of the metal. The kinetic energy of the expelled electron is equal to:

$$\tfrac{1}{2} mv^2 = h\nu - w,$$

where m and v are the mass and velocity of the photo-electron, $h\nu$ is the

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Planck—Ann. Physik **4** (1901) 553.

energy of the quantum and w is energy required to remove the electron from the atom or metal surface, i.e., work function.

$$\tfrac{1}{2}mv^2 = h\nu - h\nu_0, \quad w = h\nu_0.$$

By connecting a positive potential to the surface of the metal, Millikan was able, 1916, to measure the potential which is just sufficient to stop the ejection of electrons. The force of attraction is then equal to the kinetic energy of the electrons.

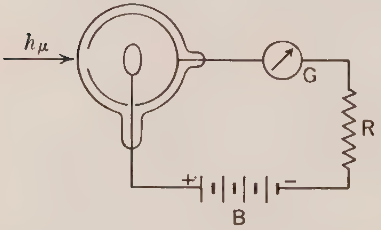

FIG. 198. Diagram of Photoelectric Cell.

$$Ve = \tfrac{1}{2}mv^2$$

or

$$\tfrac{1}{2}mv^2 = Ve = h\nu - w.$$

In this formula V is the potential difference in electrostatic units, e is the charge of the electron in electrostatic units (4.77×10^{-10}), $h\nu$ is the energy of incident radiation and w is the energy required to bring the electron to the surface of the metal. On the basis of the above equation, the energy and velocity of the ejected electron is proportional to the frequency of light. The number of photoelectrons emitted varies directly as the light intensity.

Electron velocities are often expressed in terms of volts. The electron-volt is defined as the energy of an electron that has fallen through a potential difference of one volt.

ENERGY OF PHOTON

Electric lamp	2	electron-volts
X-rays	$2 \times 10^4 - 1 \times 10^5$	" "
Gamma rays	2.5×10^6	" "

Spectra.—Newton showed in 1776 that white light was a mixture of colors by passing a beam through a prism. Light of shorter wave lengths, as violet, was refracted more than light of the longer wave lengths, as red.

In 1858 Bunsen and Kirchoff designed the first practical spectroscope. By use of this instrument the spectra of the various elements could

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EINSTEIN—Ann. Physik **17** (1905) 1932; **20** (1906) 199.
MILLIKAN—Phys. Rev. **7** (1916) 362.
HUGHES—Bull. Nat. Res. Council 2, Part 2, April (1921).
MILLIKAN—The Electron, University of Chicago Press (1924).

be examined. Two types of spectra were observed: line spectra and band spectra. Line spectra are produced by the activation of atoms and molecules in a vapor or gas. Gases may be activated to luminescence by means of discharge tubes. Metals are partially vaporized when used as electrodes for spark and arc discharges. Compounds can be heated in a flame or placed in cored electrodes. Band spectra may be considered as a series of lines very close together.

Line spectra are of two kinds: Adsorption spectra—produced by passing light from a continuous spectrum through a body of gas. Frequencies capable of being absorbed by the electrons in atoms will be observed as dark lines which are characteristic for each element. These lines are similar to the Fraunhofer lines in the solar spectrum. Emission spectra are observed as bright lines when an element radiates light. The bright lines occupy the same positions as do the dark lines in the adsorption spectrum. However, emission spectra always contain more lines than adsorption spectra.

Balmer Series of Hydrogen Spectra.—In 1885, Balmer found that wave lengths for the visible spectrum of hydrogen could be expressed by the formula:

$$\lambda = 3645 \frac{n^2}{(n^2 - 4)}$$

where λ is in Angstroms and n is a whole number equal to or greater than 3, i.e.:

$n = 3 \; \lambda = 6560$ A $H\alpha$ line red,
$n = 4 \; \lambda = 4860$ A $H\beta$ line blue.

Soon afterward Rydberg found it more convenient to represent the lines of the Balmer series in terms of frequency rather than in wave lengths.

$$\nu = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right).$$

The above formula represents the Rydberg equation in which the frequencies of the successive lines of the Balmer series are obtained when $n_1 = 2$ and n_2 is 3, 4, 5, 6, etc. R is the Rydberg constant which has a frequency value equal to 3.291×10^{15} vibrations a second.

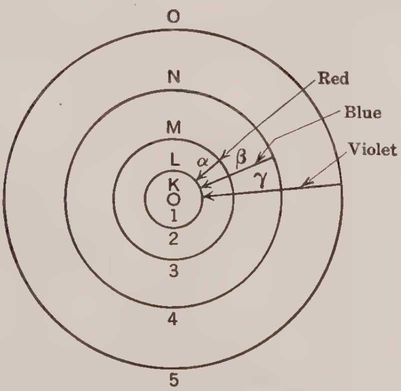

FIG. 199. Emission Spectrum of Hydrogen Balmer Series.

Since this equation gave large numbers, Ritz suggested the use of wave numbers instead of frequency.

$$\nu = \frac{c}{\lambda};$$

therefore ν is proportional to $\frac{1}{\lambda}$;

then $$\nu^1 = \frac{1}{\lambda},$$

where ν^1 is the number of waves per second, or wave number. The new formula is known as the Balmer-Ritz equation and is obtained:

$$\nu^1 = N\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right);$$

N is a constant equivalent to the Rydberg constant since $\nu = c\nu^1$ and has a value equal to 109,700 cm.$^{-1}$.

Following the discovery of the Balmer series, five other series of hydrogen spectra have been found. The position of the various lines may be calculated by means of the Rydberg formula.

Series	n_1	n_2	*Region*
Lyman	1	2, 3, 4, 5, 6	ultra-violet
Balmer	2	3, 4, 5, 6	visible
Paschen	3	4, 5, 6	infra-red
Brackett	4	5, 6	far infra-red
Pfund	5	6	far infra-red

X-ray Spectra.—Barkla, 1911,[1] studying the scattering of x-rays, found that each element irradiated with x-rays emits both hard and soft x-rays which are characteristic of the element. The hard rays were designated by the letter K and the soft rays by the letter L. The characteristic L rays consist of lines in a second spectrum and have wave lengths longer than those of the K spectrum.

Having discovered that x-rays undergo reflections at crystal surfaces, W. L. and W. H. Bragg, in 1912, built the x-ray spectrometer.[2] With the aid of this instrument they were able to discover several orders of x-ray spectra.

[1] Barkla, *Phil. Mag.* **21** (1911) 648.

[2] Bragg, *Phil. Mag.* **24** (1912) 1024; **27** (1914) 703.

Mosely, in 1913, succeeded in photographing characteristic x-ray spectra for a number of elements. He showed that the penetration of x-rays generated by targets of different metals is a linear function of the element when arranged in the order of increasing atomic weights. As the atomic number increased, the series of lines constituting the x-ray spectrum shifted toward the shorter wave lengths. Elements having high atomic numbers were found to have two additional series. The series were designated by the letters K, L, M.

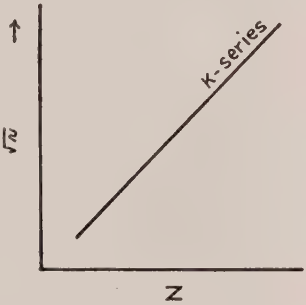

Fig. 200.

By plotting the square root of the frequency, as the α line of the K series, for the different elements against the atomic number, Mosely obtained a linear function which is represented by the following equation:

$$\sqrt{\nu} = a(Z - b).$$

in which Z is the atomic number and a and b are constants.[3]

Structure of Atom.—Based on studies in radioactivity dealing with the deflections of Alpha particles, Rutherford, 1911,[4] was the first to suggest the nuclear theory of atomic structure. The atom, according to this theory, is a miniature solar system in which a number of positive charges (protons) are packed closely together in a nucleus at the center of an atom. Surrounding the nucleus at various distances are a number of negative charges (electrons) which are equal in number to the positive charge in nucleus. Thus, an atom of an element having the atomic number Z has Z electrons each carrying a negative charge $-e$, and a nuclear charge, $+Ze$. The result of the whole represents a neutral atom.

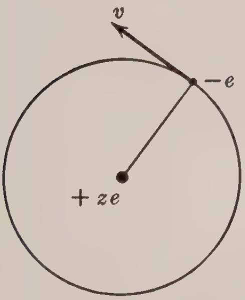

Fig. 201. Rutherford Model of Hydrogen Atom.

The Bohr Atom.—By making use of Einstein's photo-electric equation and Rutherford's atom as a model, Bohr was able, in 1913,[5] to extend the quantum theory to the interpretation of spectra obtained from hydrogen. With this theory he was able to derive the value of the Rydberg constant and the formula for the Balmer series of hydrogen.

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[3] Moseley, *Phil. Mag.* **26** (1913) 210; **27** (1914) 703.

[4] Rutherford, *Phil. Mag.* **21** (1911) 669.

[5] Bohr, *Phil. Mag.* **26** (1913) 1, 476, 857.

By rearranging the Einstein equation into the form

$$\nu = \frac{\frac{1}{2} mv^2 + w}{h}$$

and substituting frequency ν for wave number, ν^1 in the Ritz equation

$$\nu^1 = A - B.$$

Bohr showed that both equations could be written in the form

$$\nu = \frac{\text{Energy}}{h}$$

for $\frac{1}{2}$ mv is kinetic energy of the electron and W is the work function or energy required to bring the electron to the surface of a metal. Thus:

$$\nu = \left(\frac{W_2}{h}\right) - \left(\frac{W_1}{h}\right),$$

where W_2 and W_1 are energies. Then:

$$h\nu = W_2 - W_1.$$

According to Bohr's theory, the electrons of an atom may exist in different energy levels—E_1, $E_2 \cdots E_n$, without emitting or absorbing energy, but when an electron jumps from one level to another, E_2 to E_1, a quantum is absorbed or emitted and the energy of the atom changes from W_2 to W_1.

$$h\nu = W_2 - W_1$$

or

$$h\nu = E_2 - E_1.$$

Bohr assumed that the electron can revolve about the nucleus in any one of a set of particular orbits without radiating energy. Bohr further assumed that for an atom to be in a state of equilibrium, the centrifugal force must be equal to the force of electrostatic attraction between the nucleus and the electron,

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2}$$

and that the angular momentum of the electron in each orbit is a some distance; an etched parabola for use at shorter distances, and two others spreading the light over angles of 45° and 60° respectively. The reflectors are supported on light weight folding stands, or suspended from the wall and nest together for convenience in carrying.

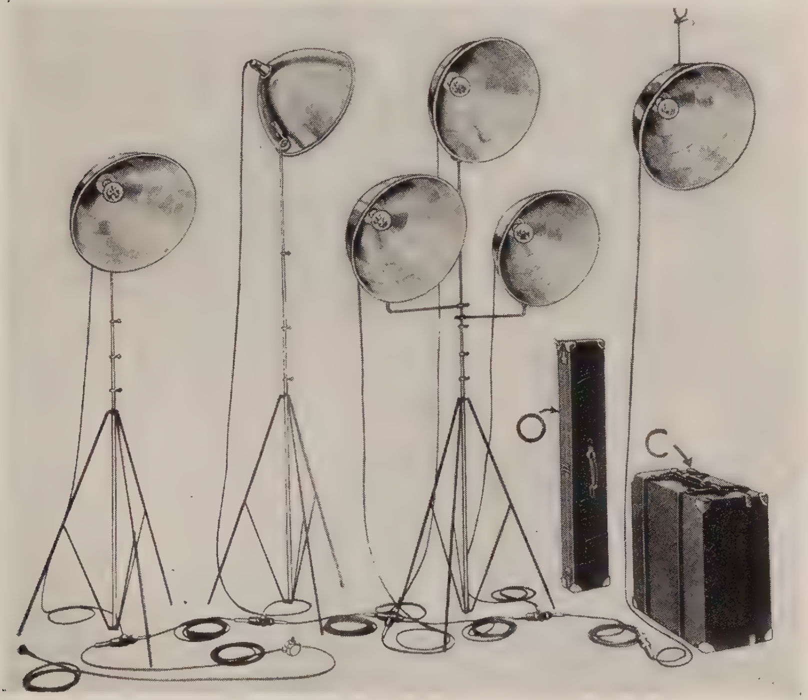

FIG. 180. Portable Lighting Equipment for Incandescent Lamps. (Johnson Ventlite Company.)

Arc Lighting Equipment.—A typical floodlighting unit employing a twin arc is shown in Fig. 181. The twin arc is generally preferred over the single since, with practically the same current consumption, the light intensity is nearly twice as great. An electrical relay mechanism controls the positions of the carbons so that the lamp requires no attention except when it is necessary to change the carbons. Automatic operation also results in a light source, which is more nearly constant in intensity. For floodlighting, the arcs are invariably enclosed in a box-like cabinet and in some cases, deflectors are provided to cover the arc so that only the light reflected from the sides of the cabinet is used.

The arc, being essentially a point source of light, is well adapted to spotlighting requirements. Spotlights employing an arc source do not, in general, differ essentially in design from those already described.

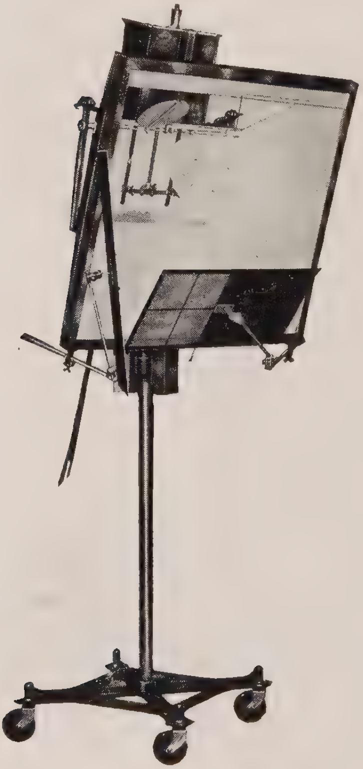

Fig. 181. Typical Arc Lamp for Portrait and Commercial Photography. (Photogenic Machine Company.)

Equipment for Fluorescent Lamps.—Fluorescent lamps, being an extended, highly diffuse source of light, have been used chiefly, up to the present time, in portraiture. A typical unit (Fig. 182) consists of a number of lamps, each with a trough-like reflector in a frame mounted on a stand, which enables the lighting unit to be raised or lowered as required. Similar lighting units are available for permanent installation on the studio walls, and small units with collapsible stands are available for home portrait work.

Care of Lighting Equipment.—Lamps or reflectors should be kept clean. Even in a comparatively clean district there is enough dust, smoke and soot in the air to justify regular cleaning of the lighting equipment once a month. In the downtown sections of a busy industrial city, or in close proximity to smoke and dust producing plants, more frequent attention is required. Clean lamps and reflectors with soap and water or a soft cleaning powder. Light diffusing materials, such as tracing cloth, china silk, and buckram, should be renewed every six months.

To obtain maximum efficiency from the light, the walls of the studio should be painted white, light ivory, or light gray. If the walls are dark, little light is reflected and practically all of the illumination comes directly from the lighting units; if the walls and ceiling are light, the light reflected provides illumination for the shadows and reduces the exposure.

Incandescent lamps should be burned at their stated voltage. If the voltage is too high, the lamps burn brightly but their life is unduly shortened. If the voltage is too low, the light output is greatly reduced and the actinic intensity of the light is reduced even more. Therefore, it pays to make certain that the rated voltage of the lamp corresponds with the actual voltage at which they are used.

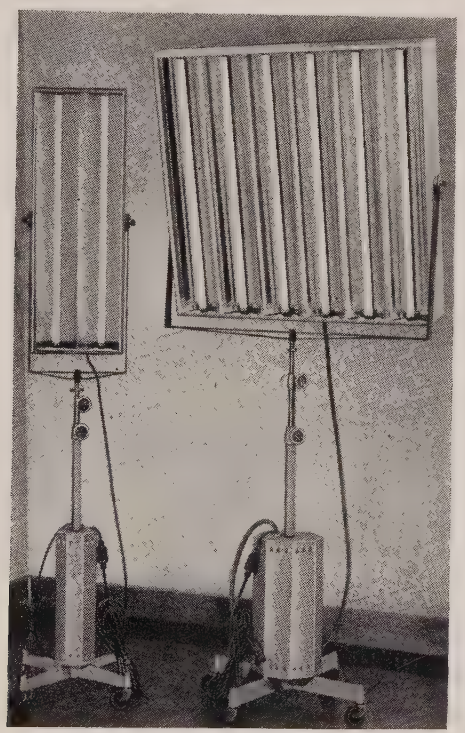

FIG. 182. Lighting Unit Employing Fluorescent Lamps. (Johnson Ventlite Company.)

It is distinct economy to use, in each lighting unit, only the particular size and type of lamp for which the unit is designed. This is especially important in the case of spotlights and focusing reflector floodlights, both of which depend for efficient illumination upon the light source being in the proper position with respect to the optical system.

All electrical wiring, cords, switches, connections, etc. should be checked periodically and repaired or replaced at first sign of disorder to prevent possible damage to equipment, injury to operators, or fire danger.

Reflecting and Diffusing Mediums.—Reflectors increase the effective candle power of a light source by directing it towards the area to be illuminated. The reflector should, so far as possible, confine the light to the area to be illuminated; reflectors which spread the light over a larger area are wasteful of light. Specular surfaces form the most efficient reflectors, but are more costly to produce, and the surface is not as permanent or as resistant to wear. In addition, difficulty is frequently experienced in obtaining uniform illumination, owing to the imaging of the light source. Matt or semi-matt surfaces, which reflect diffused light, are preferable for most purposes.

The efficiency of a number of the materials used in the construction of reflectors for photographic lighting equipment is shown in the following table:[8]

Surface	*Character of Reflected Light*	*Per Cent Reflectance*
Silver plate	Specular	85–90
Glass mirror	Specular	80–90
Aluminum foil	Specular	85
Aluminum, Alzak	Specular	75–85
Aluminum, polished	Diffuse	70–80
Aluminum, oxidized	Specular	60–70
Aluminum, etched	Diffuse	70–85
Chromium	Specular	60–65
Chromium, satin	Diffuse	50–55
Stainless steel	Specular	55–65
Stainless steel, satin	Diffuse	50–55
Porcelain enamel, white	Diffuse	60–80

The effect of the reflecting surface on the spectral energy distribution of the reflected light is manifestly of importance in color photography, but no data appears to be available on this point.

Light Diffusing Materials.—Light diffusing material should diffuse or spread the light with as little absorption as possible. In the ideal case, the entire surface of the diffusing material should be uniformly illuminated and should appear equally bright when viewed from various directions. Such uniformity is extremely difficult of attainment, but the translucent materials at present available, when used in conjunction with properly designed reflecting equipment or several lamps correctly spaced, give a sufficient uniformity to meet photographic lighting requirements. Data on the more common types of translucent materials are given in the following table:

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[8] Compiled from data supplied by Nela Park Engineering Department, General Electric Company.

Materials	*Per Cent Light Transmitted*	*Diffusing Properties*
Tracing Cloth	60–70	Good
China Silk	60–70	Fair
Acid-Etched or Ground Glass	85–90	Good
Enamel-Coated Glass	20–30	Excellent
Rippled Glass	80–90	Fair

Flash Lamps.—In the latter part of 1930 the General Electric Company announced the first Photoflash lamp to appear on the American market. This lamp contained about 65 mg. of thin aluminum foil which was ignited by passing an electric current through a filament covered with a chemical primer. The bulb was filled with oxygen to a pressure of 170 mm. of mercury. This lamp gave a flash of relatively short duration (about 1/50 sec.) and of sufficient intensity to properly expose a subject under average indoor conditions.

Immediate acceptance of this lamp was inevitable since it abolished the fire hazard ever present with the open firing of magnesium powder and introduced a controlled light source thereby eliminating one of the variables of indoor picture taking. Amateurs used the lamp by the so-called " open flash " technique; i.e., they opened the shutter on " time," flashed the lamp to make the exposure, then closed the shutter. By this method satisfactory pictures could be taken of stationary or slow moving subjects simply by allowing the duration of flash of the lamp to control the exposure interval. In the early thirties many devices, known as synchronizers or flash guns, were introduced to synchronize the opening of between-the-lens shutters with the peak intensity of the flash in an effort to make possible flash photography at the higher shutter speeds. At the same time the lamp manufacturers attempted to standardize the time characteristics of their flash lamps so that the light emitted would reach maximum brilliance in 20 milliseconds[9] after the primer filament had been energized.

The duration above half peak intensity for the early foil-filled lamps was approximately 1/120 sec. This short duration made it rather difficult to synchronize the camera shutter at the higher shutter speeds, so that it would be open during this relatively short interval. To overcome this condition, the foil filling was replaced with a wire filling which burned at peak brilliance for a longer interval, thereby producing a lamp with a duration above half peak intensity of about 1/60 sec. Both leaf foil, shredded foil and wire-filled lamps are available today. The foil-filled lamp usually reaches a higher peak intensity than a wire-filled lamp of corresponding bulb size, while the wire-filled lamp gives a flash of somewhat lower peak intensity but of longer duration.

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[9] A millisecond is 1/1000 sec.; therefore 20 m.s. = 1/50 sec.

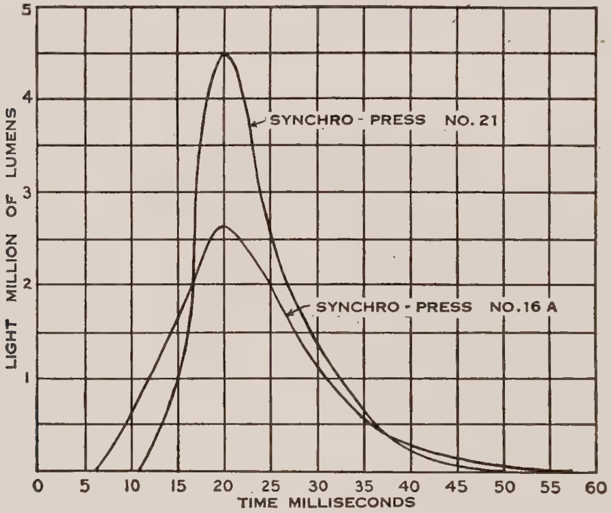

Fig. 183. Time-Light Curve of Nos. 16 A and 21 Flash Lamps.

Fig. 183 gives comparative time-light curves for the No. 16A Photoflash lamp, which is wire filled,[10] and the No. 21 lamp which is foil-filled. The following characteristics should be noted:

Lamp	No. 16A	No. 21
Filling	Shredded foil	Leaf foil
Peak Intensity, lumens	2,600,000	4,500,000
Duration of Flash above half peak intensity, m.s.	9	14
Time to Peak Intensity	20	20

A third type of flash lamp is available which permits synchronization with focal plane shutters. This is a wire filled lamp having a still lower peak intensity but with a very prolonged flash. Fig. 184 shows the time-light trace for the No. 6 and No. 31 focal-plane lamps. This

[10] The wire filling in Mazda Photoflash lamps is referred to as shredded foil since the filling is made by shredding foil into thin wire-like strips.

long flash is needed so that light of constant intensity will be incident upon the subject throughout interval required for the focal-plane shutter slit to traverse the film. The No. 6 lamp is intended for use only with focal-plane cameras of the miniature type.

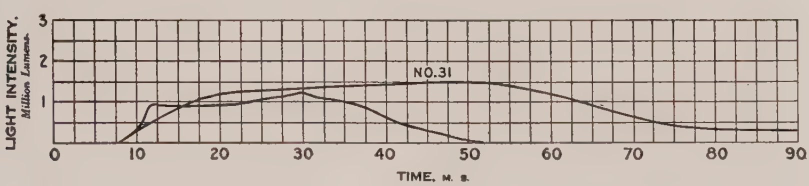

FIG. 184. Time-Light Curves for the Nos. 6 and 31 Flash Lamps for Synchronization with Focal Plane Shutters.

Flash Lamp Characteristics.—The following characteristics of a flash lamp should be known to describe fully its photographic usefulness as a light source:

1. Spectral quality of the radiation.
2. Total quantity of light emitted, *lumen-seconds.*
3. Maximum intensity of the radiation, *lumens.*
4. Time from application of the filament current to the *start* of the flash, m.s.
5. Time from application of the filament current to the *peak intensity* of the flash, sec.
6. Total *duration* of the flash above a specified minimum intensity, sec.

The time characteristics (Items 4, 5, and 6 above) can be readily determined by passing light from the lamp through a slit onto a sheet of film which is moved past a slit with a known velocity. A study of the variation in density of the resulting photographic trace gives a measure of the "photographic effectiveness" of the radiation directly as a function of time. A spark discharge flashed through the slit at the instant the filament circuit is closed records the zero point from which to make time measurements. Fig. 185 shows a density-time trace for a No. 5 Photoflash lamp which was obtained by exposing a 4 × 5 inch sheet of film in the G. E. Synchrograph shown in Fig. 186. This instrument consists of a rotatable drum in which is cut a longitudinal slit. Surrounding the drum is a light tight chamber which holds the film in a cylindrical shape of slightly greater radius than that of the drum. Light from the flash lamp enters the hole at one end of the synchrograph where it is spread by a conical mirror into a disc of light orthogonal to the axis of the drum. By rotating the drum at a known r.p.m., light from the lamp passes through the slit onto the film to expose the density trace of the lamp. Light from a momentary spark discharge which is flashed simultaneously with the closing of the lamp filament circuit enters the other end of the synchrograph, is deflected by a second conical mirror, and passes through the drum slit to establish the zero reference line shown in Fig. 185.

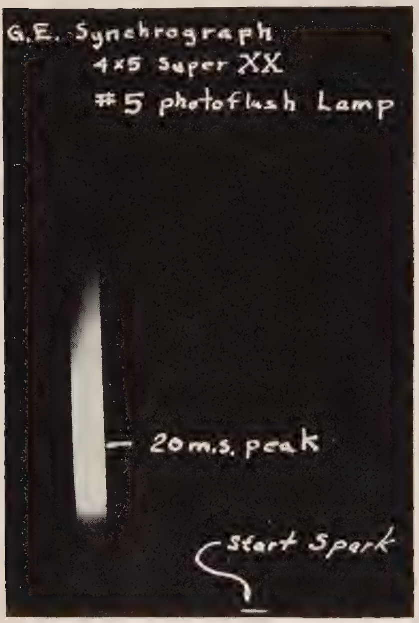

Fig. 185. Synchrograph Trace of No. 5 Lamp.

Intensity measurements for flash lamps can easily be obtained by allowing the light from the lamp to fall upon the surface of a photo tube which is connected through a suitable amplifier to a string oscillograph. Time-light curves obtained in this manner are shown in Fig. 187. The wavy character of the time-light curves is caused by superimposition of the trace of a 1000-cycle tuning fork onto the time-light curves. This procedure gives a convenient

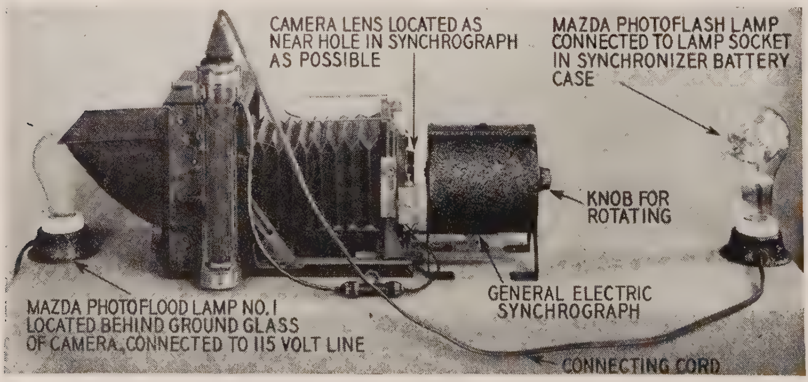
CAMERA LENS LOCATED AS NEAR HOLE IN SYNCHROGRAPH AS POSSIBLE
MAZDA PHOTOFLASH LAMP CONNECTED TO LAMP SOCKET IN SYNCHRONIZER BATTERY CASE
KNOB FOR ROTATING
GENERAL ELECTRIC SYNCHROGRAPH
MAZDA PHOTOFLOOD LAMP NO. I LOCATED BEHIND GROUND GLASS OF CAMERA, CONNECTED TO 115 VOLT LINE
CONNECTING CORD

Fig. 186. General Electric Synchrograph.

method of measuring time along the curve, since the time between each peak of the tuning fork disturbance is exactly one millisecond. Curve 5 (Fig. 187) is for a No. 11 lamp operated with two 1½ volt D cells having a short circuit current of 5 amps. It will be noted that under these conditions the lamp reaches peak intensity in 20 milliseconds after the current is applied. Curves 4 and 3 are for No. 11 lamps when fired with two 1½ volt D cells with short circuit currents of 4 and 3 amps respectively. It is apparent that the weaker batteries slow down the lamp materially. For these tests the lamps were flashed in a Kodak Senior Synchronizer (see Page 196) which has an electromagnet of 2.4 ohms resistance connected in parallel with the lamp. The ordinate values for these time-light curves are found by calibrating the oscillographic equipment against a standard incandescent lamp of known brightness and color temperature.

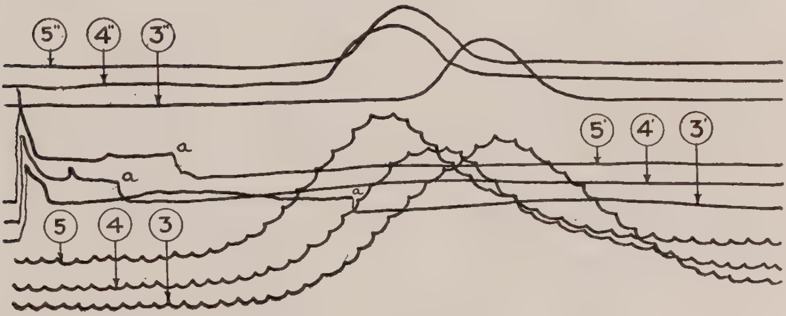

Fig. 187. Oscillograph Tracings of a No. 11 Flash Lamp.

Curves 5′, 4′, and 3′ in Fig. 187 show the current through the lamp filament and the time to filament burn out for each case. It will be observed that the filament current rises sharply at the instant the circuit is closed but drops to a steady value within one to two milliseconds. The sharp break in the current trace at point A shows where the filament burned out. It is apparent that the time to filament burnout is greatly prolonged by using weak batteries.

Spectral Distribution of Flash Light.—The spectral character of a light source having a continuous spectrum may be specified conveniently by giving the color temperature of the source. The color temperature is defined as the temperature to which a black body must be raised so that the light it emits has the same integral color as that

TABLE 1. CHARACTERISTICS OF MAZDA PHOTOFLASH LAMPS *

Lamp No.	*SM++*	*5*	*5B*	*11*	*16A*	*21+*	*21B+*	*22*	*50*	*75*	*6*	*31*
Bulb	B11	B11	B11	A15	A17	A19	A19	A19	A21	PS35	B11	A21
Bulb volume (cc)	25	25	25	70	95	140	140	140	190	800	25	190
Total light output in lum.-sec.	5,000	18,000	6,000	30,000	43,000	50,000	17,000	65,000	110,000	160,000	18,000	75,000
Max flux in million lumens	0.8	1.2	0.4	2.4	2.6	4.5	1.6	4.0	5.5	9.5	0.5	1.5
Time in sec. from close of circuit to:												
Peak of flash †	0.005	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.030	0.035–0.040		
One-half max. int.†	0.0035	0.015	0.015		0.014	0.016			0.023		0.012	0.015
Filament burn-out†	0.0015	0.0025	0.0025	0.0020	0.0025	0.0015	0.0015	0.0015	0.0015		0.0015	0.0015
Effective duration of flash (sec.)‡	0.0035	0.012		0.015	0.015	0.010			0.013	0.010	0.030	0.055
Color temp, °K	3300	3800	6300	3800	3800	3600	6300	3800	3800	3450	3800	3800

* Measurements made in Lamp Development Laboratory, Nela Park, Cleveland, Ohio.

† Lamps flashed on 3 Type D cells.

‡ Approximate duration of light intensity above a half million lumens.

+ No. 21 and No. 21B lamps leaf foil-filled.

++ SM lamp has no filling; all others shredded foil-filled.

of the source being considered. Thus, for example, if a flash lamp has a color temperature of 3600° K, it means that the light from the lamp has the same integral color as that from a black body operated at a temperature of 3600° K. The color temperature of a flash lamp is usually specified for only that light having an intensity above a half million lumens to avoid the light emitted at the beginning and end of the flash where the temperature of the aluminum filling is rising or falling.

The table on Page 190 gives the operating characteristics of G. E. Photoflash Lamps, including the color temperature for each lamp. It will be noted that all of these lamps operate at a color temperature lying between 3450° K. and 3800° K. except the No. 5B and No. 21B lamps which are specially coated with a blue lacquer to raise the color temperature to 6300° K. so that it will be a suitable source for use with Kodachrome film balanced for daylight use.

Since both orthochromatic and panchromatic emulsions can be exposed by either daylight (5400° K. upwards) Photoflood light (3400° K.), or regular tungsten lamps (2850° K.), it is apparent that these emulsions can be exposed properly with any Photoflash source which has a color temperature lying between these limits.

The following table will be found helpful in selecting the proper filter to use when exposing Kodachrome Films by Photoflash light:

	Kodachrome Type A	*Professional Kodachrome Type B*
Leaf Foil Filled Lamps	CC-13	CC-15
Wire or Shredded Foil Filled Lamps	CC-15	2 A

The Photoflash lamps listed in this table (except the No. 5B and No. 21B) can be used in this manner with Kodachrome Films balanced for tungsten illumination.

Kodachrome film (daylight type) requires a much bluer light than that emitted by regular flash lamps since this film is balanced to give proper color rendition by daylight (5400° K.). The No. 21B and No. 5B lamps are coated with a blue lacquer which was developed by the Kodak Research Laboratory and has such a transmission that the light from the bulb is of the proper color temperature to supplement daylight in taking pictures with Kodachrome film balanced for daylight. Fig. 188 compares the spectral transmission of the blue lacquer with that of an ideal filter that would transform light from a No. 21 or 5 lamp to a color temperature of 6500° K., which is within the range of color temperature of the light for which this type of Kodachrome film is balanced.

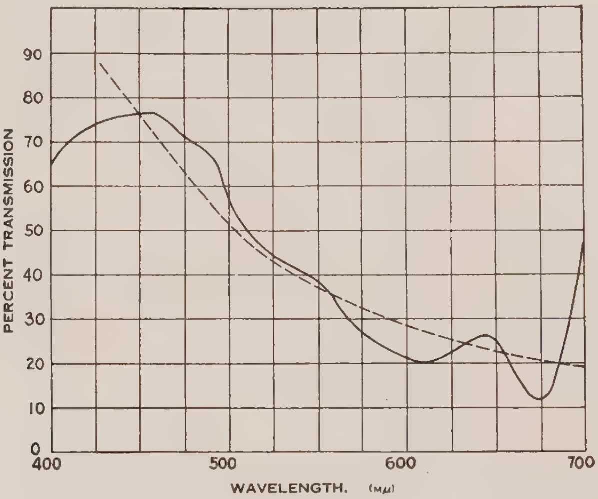

FIG. 188. Spectral Transmission of Lacquer Used on Nos. 5B and 21B Lamps.

Synchronization.—Manually set camera shutters, such as the Supermatic, Kodamatic, Diomatic and Compur, require about 5 milliseconds for the shutter blades to reach the full open position; i.e., 5 milliseconds elapses between the instant when the shutter is tripped and the shutter blades open fully. The duration of the interval during which the shutter remains open depends upon the shutter speed. The following table gives average values for the duration of full shutter opening for several shutter speeds. Fig. 189 shows a graphical record of these shutter characteristics together with a trace of the time-intensity curve of a typical flash lamp which was energized at the

Shutter Speed	*Time for Shutter Blades to Reach Full Opening, m.s.*	*Duration of Full Opening, m.s.*	*Total Elapsed Time between Tripping Shutter and Closing of Blades, m.s.*
1/400	5	2.5	8.5
1/200	5	5	11
1/100	5	10	16
1/50	5	20	26

same instant that the shutter was tripped. From this record it may be seen that no light from the lamp passed the shutter at either the 1/400 or 1/200 speeds, and that an insufficient percent of the total light reached the film at the 1/100 speed. Hence we may conclude that simultaneous flashing of the lamp and tripping the shutter would give satisfactory results only for those shutter speeds slower than 1/100 second.

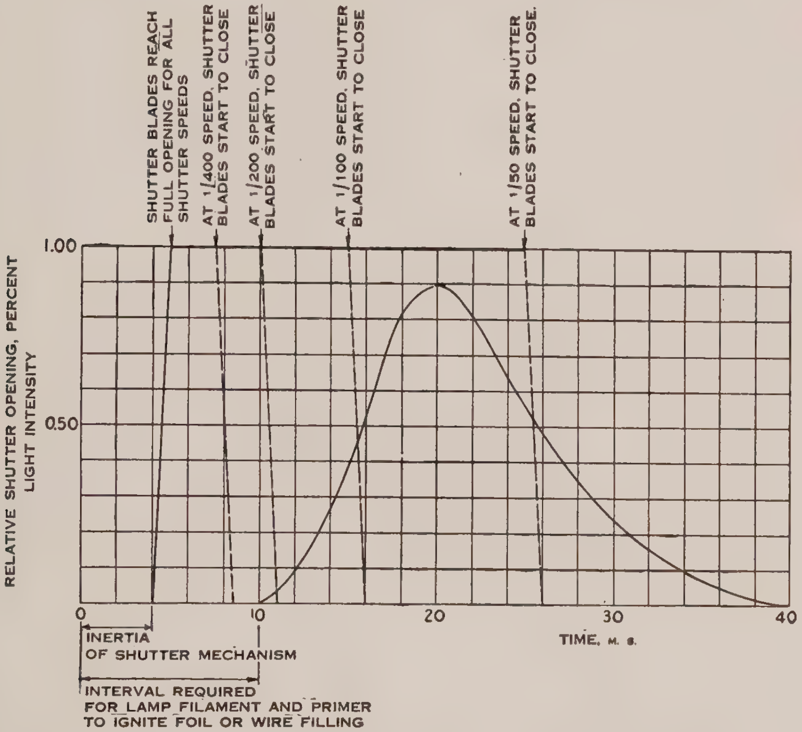

FIG. 189. Shutter and Lamp Curves Showing Timing when Lamp is Flashed at Instant of Tripping Shutter.

To overcome this difficulty various synchronizing devices have been made which delay tripping the shutter until 12 to 15 milliseconds after the lamp circuit is closed. In this manner the shutter action is retarded sufficiently to allow the lamp to almost reach peak intensity before the shutter blades reach the full open position. A graphical representation of a properly synchronized shutter is shown in Fig. 190. It will be seen that when the shutter action is sufficiently retarded it is possible to take pictures at any desired shutter speed since ample light is passed by the shutter at all speeds.

Self acting shutters, such as the Kodex and Dakon, require about 13 to 15 milliseconds to reach the full open position. For this reason, a delay type synchronizer mechanism is not required for these shutters since flashing the lamp at the instant the shutter is tripped results in the shutter blades being fully open during the peak intensity of the lamp. Self acting shutters in general do not have shutter speeds greater than 1/100 sec.; therefore the blades remain fully open for a sufficient duration to pass ample light from the flash to the film.

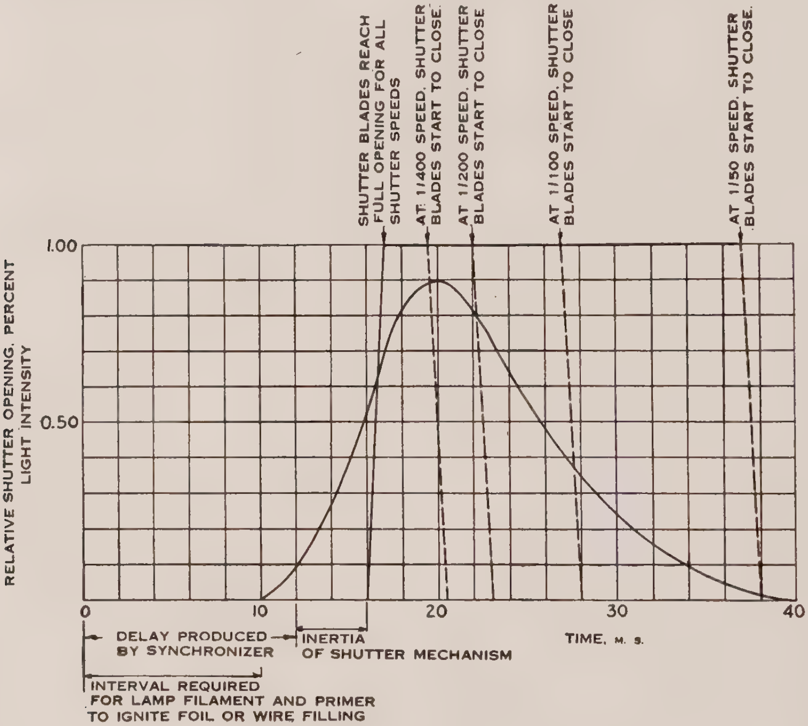

FIG. 190. Shutter and Lamp Curves for Properly Synchronized Shutter.

Synchronizers.—Devices for synchronizing the shutter action with the flash of the lamp may be divided into two types: (1) mechanical synchronizers and (2) electromagnetic synchronizers.

The Kalart Micromatic Speed Flash, shown in Fig. 191, is representative of one of the better mechanical synchronizers in popular use today.

The synchronizing device, which attaches directly to the camera shutter, is electrically connected to a suitable battery case which accepts the flash lamp and holds a reflector to direct light from the lamp toward the subject. In operation, a disc within the synchronizer housing is manually rotated against the action of a helical spring until a small pawl engages the disc, holding it in the "cocked" position. When pressure is applied to the cable release, the pawl is depressed and a flat silver spring makes contact against a screw which is connected to one of the lead-in wires to the battery case. The helical driving spring is always in contact with the wall of the synchronizer housing to which the other lead-in wire is grounded. Thus, when the cable release is pressed, the action of the pawl causes the electrical circuit to be completed thus firing the lamp.

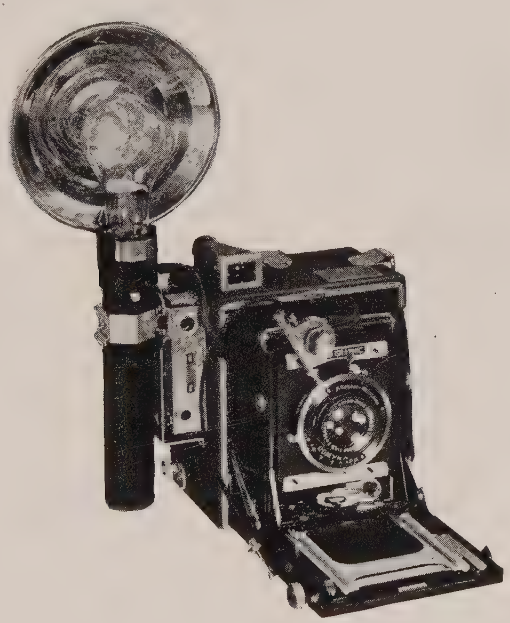

Fig. 191. Kalart Micromatic Speed Flash Synchronizer.

The disc then starts in motion, actuated by the tension of the helical spring. After about 12 to 15 milliseconds of rotation, the disc reaches a position where it allows a small spring-driven plunger to enter the shutter with just sufficient force to trip the shutter. From this explanation it is seen that the electrical circuit is closed when the pawl is pressed by the cable release sufficiently to free the spring driven disc which, 12 to 15 milliseconds later, releases the plunger to trip the shutter.

With mechanical synchronizers the electrical energy supplied by the battery is used only to raise the filament of the flash bulb to incandescence. The circuit is automatically broken when filament burnout occurs. Because of this, each flash lamp fired drains but a negligible amount of energy from the batteries, and consequently long battery life results. Considerable care must be exercised in the design and manufacture of the moving contacts employed in mechanical synchronizers, since high contact resistance or vibratory erratic contact will seriously delay the time to peak intensity of the lamp. Some mechanical synchronizers are so made that the tripper mechanism is influenced by the rapidity with which the operator presses the cable release. Devices of this nature cannot be free from the subjective effect of the operator, and therefore are not as reliable as a device which completes its cycle of operations in a predetermined manner.

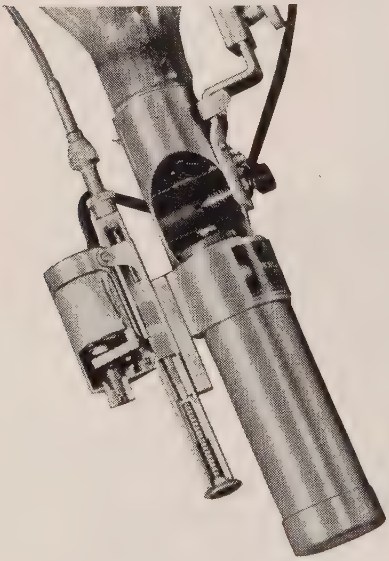

Fig. 192. Cut-away Model of Kodak Senior Synchronizer, Speedgun Model E.

Fig. 192 shows a cut-away view of the Kodak Senior Synchronizer, Speedgun Model E. This is a typical electromagnetic synchronizer which operates the camera shutter through a cable release. In operation a spring loaded plunger is manually moved to the "cocked" position (as shown in Fig. 192) where it is held by a small pawl. When the synchronizer switch is pressed both the lamp and electromagnet circuits, which are connected in parallel, are closed simultaneously. The air gap in the magnetic circuit of the solenoid is adjusted to allow about 12 milliseconds to elapse before sufficient flux density is built

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Morgan—Synchroflash Photography. Morgan & Lester, Publishers, New York.

up to withdraw the pawl and thereby release the plunger. When the plunger is released it travels upward under the action of the spring striking the end of the cable release which in turn trips the shutter.

By proper coil design, i.e., correct balance of resistance, ampere-turns, and magnetic reluctance, it is possible to have both the lamp and shutter remain in matched synchronization throughout a wide range of battery amperage. The curves shown in Fig. 190, Page 194, illustrate this condition for new batteries having a short circuit current of 5 amperes to practically exhausted batteries having a short circuit current of but 3 amperes. These curves show that while the lag of the lamp is increased as the batteries age, the action of the coil is slowed up so that the shutter opening is also delayed by a corresponding amount.

If the coil of a magnetic synchronizer has a resistance much below 2 ohms it will drain too much current from the batteries and consequently slow down the flashing of the lamp. Electromagnetic synchronizers of this type are very sensitive to changes in battery amperage and are quickly thrown into malsynchronization as the batteries age.

Multiple Flash.—Frequently photographers wish to synchronize more than one flash bulb with the camera shutter in order to obtain better subject modeling than is possible with a single light source. These extension flash lamp sources are wired in parallel to the lamp socket on the synchronizer battery case. The added resistance of this wiring and the resistance of the contacts should not be greater than 0.5 ohms; otherwise the time lag of the lamps will be increased more than is allowable for synchronization. The effect of circuit resistance upon the timing of the lamps is shown in the table below.

EFFECT OF RESISTANCE ON TIMING OF PHOTOFLASH LAMPS FLASHED ON 3 VOLTS (TWO TYPE D DRY CELLS)

Length of No. 18 Stranded Wire Two Conductor Lamp Cord	*Time from Contact to Peak Intensity, m.s.*		
	No. 21 Lamp	*No. 16A Lamp*	*No. 5 Lamp*
0	20	20	20
25 ft.	22	21	22
50 ft.	35	22	23

Battery Resistance.—Since the internal resistance of the batteries is in series with the flash lamp at firing it is important to use batteries which have a fairly low and stable internal resistance. The small penlite cells have an internal resistance two to three times as great as that of D cells. Since the internal resistance of all batteries increases with age it is good practice to replace batteries every month, especially the smaller. The table below gives a comparison of the time to peak intensity of lamps flashed on penlite and type D cells for various voltages. It will be observed that satisfactory performance is obtained with little change in peak lag for voltages between 3 and 18 volts.

EFFECT OF VOLTAGE ON TIMING OF PHOTOFLASH LAMPS

Voltage	*Cell Type*	*Time (m.s.) from Contact to Peak Intensity*	
		No. 21 Lamp	*No. 16A Lamp*
1.5	Penlite	—	25
1.5	Type D	35	22
3.0	Penlite	23	23
3.0	Type D	20	20
4.5	Type D	19	19
9.0	Type D	19	19
18.0	Type D	18	19
110.0	A.C.	15	—

Testing Accuracy of Synchronization.—The synchronizer should be tested from time to time for accuracy of synchronization. This can be done visually with sufficient precision by the following method: Secure a three-foot extension lamp cord having a bulb socket at one end and a male plug at the other. Screw a flash bulb into the socket and insert the plug into the bulb receptacle on the synchronizer battery case. Place the bulb behind the camera with the camera back open, having no film in the camera. Set the lens at maximum aperture and the shutter at the desired shutter speed. With the synchronizer and shutter cocked, fire the synchronizer at the same time looking directly into the lens. A brilliant flash of light will be seen through the shutter if the unit is synchronized properly.

More accurate tests can be made with the G. E. Synchrograph, Fig. 186. Using a 3 foot extension cord, place the flash bulb in front of the opening at one end of the Synchrograph. Arrange the camera so that its lens is in front of the opening at the other end of the Synchrograph. Place a lighted Photoflood lamp in back of the camera with the camera back open. Connect the extension flash lamp cord to the receptacle on the synchronizer battery case. With the Synchrograph loaded with a sheet of 4 × 5 in., slowly rotate the drum of the Synchrograph and fire the synchronizer,—having previously set the lens at maximum aperture and the shutter at the desired speed. Upon development of the Synchrograph film a record similar to that shown in Fig. 193 will be obtained if the synchronizer is in proper adjustment. This testing procedure gives an exact record of the time relation between the peak light and the shutter opening.

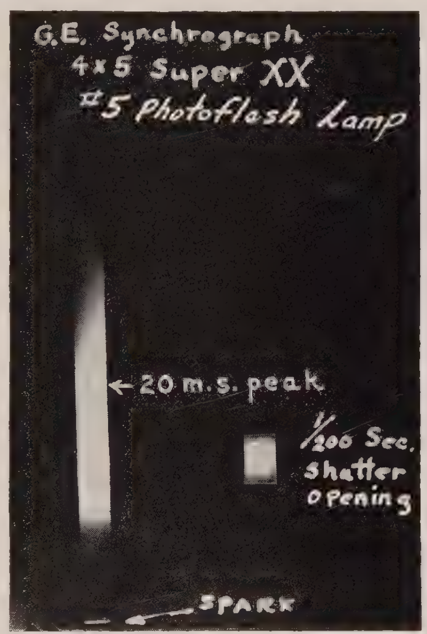


FIG. 193. Synchrograph Record of Properly Synchronized Shutter.

Reflectors.—Flash lamps are usually fired in a reflector which directs the light toward the subject. The light output values for the various Photoflash lamps given in Table I are for lamps flashed in the open without a reflector.

For the larger bulb sizes (11, 16A and 21) a properly designed portable hand-held reflector will increase the light available at the subject from 3 to 5 times that obtained with a bare lamp. Greater efficiency than this can only be obtained by flashing the lamps in studio type reflectors which are sufficiently large to collect and redistribute a higher percentage of the total radiation.

With the advent of the small No. 5 Photoflash lamp it became possible to design hand-held reflectors which give a 50° to 60° direct beam containing 5 to 9 times as much light as that emitted through this solid angle by the bare lamp. Thus because of the higher reflector efficiency made possible by the smaller bulb size, the No. 5 lamp has about the same photographic effect as the larger No. 11 lamp in a reflector of the same diameter. Recently focusing reflectors have been introduced for use with the No. 5 lamp which permit special spotlight effects at greater distances than the larger lamps.

The S. M. Photoflash Lamp.—In March 1941 the General Electric Company announced a new midget type Photoflash lamp called the

SM (Speed Midget) which has the same size as the No. 5 lamp but radically different characteristics. The SM lamp contains neither foil nor wire filling. A heavy coating of primer carried by the filament and lead-in wires burns in oxygen to produce the light emitted by the lamp.

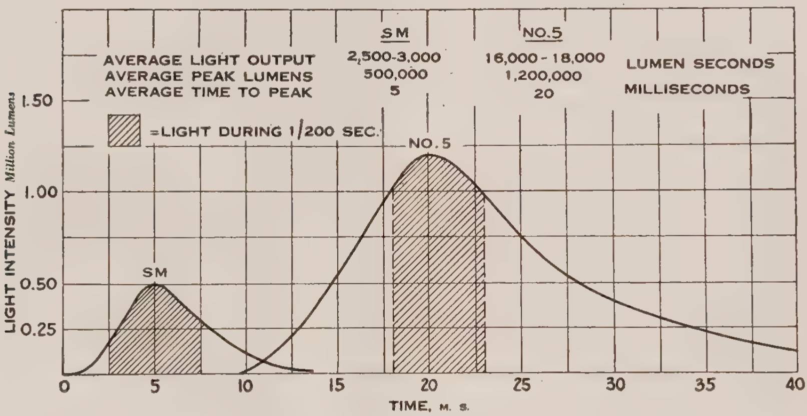


FIG. 194. Time-Light Curves for Nos. SM and 11 Lamps.

Combustion takes place so rapidly that the light reaches peak intensity in but 5 milliseconds after the filament is energized, rather than the 20 milliseconds delay required by foil and wire filled lamps. It will be recalled that manually set shutters such as the Supermatic and Compur shutters require but 5 milliseconds for the blades to reach the full open position. Therefore the synchronization of the SM lamps with these shutters may be easily obtained by firing both lamp and shutter at the same instant, thereby eliminating the necessity for any shutter delay mechanism.

The total duration above ½ intensity of the flash from an SM lamp is but 3.5 milliseconds (1/200 sec.); therefore for all shutter speeds of 1/200 and slower the flash of the lamp will control the exposure interval. The peak intensity of this lamp is about 800,000 lumens, which is sufficient for satisfactory exposures on Super XX film at 35 feet with an *f*/4.5 lens provided the lamp is flashed in a reflector having a relatively high efficiency. Fig. 194 gives a comparison between the time-light characteristics of the SM lamp and the No. 5 lamp.

Exposure Considerations.—To expose a photographic emulsion correctly by means of a synchronized Photoflash lamp source the following variables must be known and properly related:

1. Sensitivity of the film to the light emitted by the flash lamp.
2. Total quantity of light emitted by the lamp.
3. Efficiency of the lamp reflector.
4. Average reflection factor of the subject.
5. Percentage of total reflected light from the subject which is passed by the shutter.
6. f/number employed.
7. Lamp-to-subject distance.

It is common practice to publish exposure tables which specify the recommended f/number for a given lamp-to-subject distance, when using a particular film and lamp combination, at a given shutter speed. However, since exposure depends not only upon the lamp and film used, but also upon the reflection factor of the surroundings, these data should be adjusted for the actual conditions under which the pictures are being taken. This adjustment is more necessary when Kodachrome is being used, since the exposure is more critical for this film.

If a film is to be exposed properly by the light emitted from a given flash lamp, the f/number and lamp-to-subject distance must be so related that the quantity of light falling upon the emulsion surface is of sufficient magnitude to expose the film correctly. It is also important that this quantity of light be held at a constant value for all lamp-to-subject distances if uniform exposures are to be obtained.

It will be recalled that the quantity of light reaching the film varies inversely as the square of both the f/number and lamp-to-subject distance. This may be stated as follows:

$$E = k\left(\frac{1}{(f/\text{no.})^2} \cdot \frac{1}{d^2}\right), \tag{1}$$

where E = exposure received by the film,
k = a constant whose value depends upon the sensitivity of the film, the light output of the lamp, the average reflectivity of the subject, the shutter speed, and the efficiency of the reflector,
d = lamp-to-subject distance.

From Eq. 1, it will be seen that the product of the $(f/\text{no.})^2$ and $(\text{lamp-to-subject distance})^2$ must be held constant if the exposure received by the film is to remain fixed, or

$$(f/\text{no.})^2 \cdot d^2 = K. \tag{2}$$

By extracting the square root of both sides of the above equation, we may write,

$$f/\text{no.} \cdot d = \sqrt{K} = G. \tag{3}$$

The constant G is often referred to as a Guide Exposure Number.

Both film and lamp manufacturers publish Guide Exposure Numbers which are determined experimentally by taking pictures under carefully controlled conditions at all shutter speeds and with each lamp and film combination. From the proper Guide Exposure Number, the correct f/number to use at any lamp-to-subject distance may be found by substituting in Eq. 3. For example, if the Guide Exposure Number for a No. 16A Photoflash Lamp at 1/100 second with Kodak Super-XX Film is 220; at 10 feet (lamp-to-subject distance) the proper f/number would be $\frac{220}{10} = f/22$; at 20 feet, the f/number would be $\frac{220}{20} = f/11$, etc.

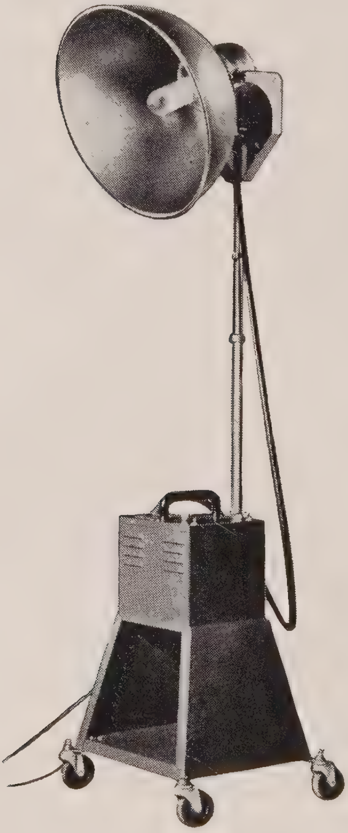


Fig. 195. Kodatron Speedlamp.

Kodatron Speedlamp.—In August, 1940, the Eastman Kodak Company announced an ultra-fast repeatable flash source which had been developed at the Massachusetts Institute of Technology by Messrs. Edgerton, Germeshausen, and Grier. This lamp, known as the Kodatron Speedlamp, produces a flash of very high actinic value and of extremely short duration. With but a single lamp, exposures can be made at $f/16$ at 20 feet with a flash duration reaching peak intensity in 1/30,000 second.

The Kodatron Speedlamp utilizes a gas-filled, electrically operated flash tube which provides an extremely high volume of soft light for photographic purposes. The Kodatron flash is produced by discharging a condenser through the flash tube. Ordinary 110-volt, 60-cycle current is led into the power unit of the lamp where a specially constructed transformer steps it up to 2000 volts. This current is then rectified and charges a condenser from which it is discharged through the gas-filled tube. The flash is of high intensity but of short duration and not at all disturbing—in fact, one scarcely sees the flash. The Kodatron Speedlamp, Fig. 195, consists of a power unit mounted in a

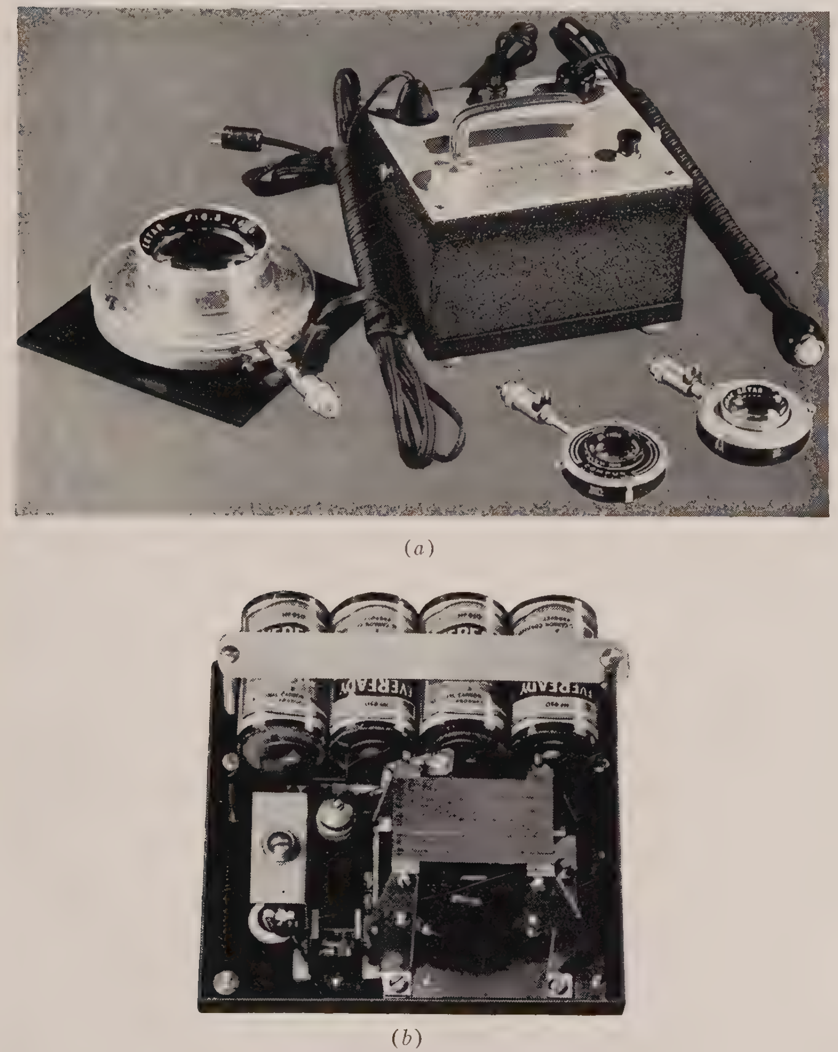
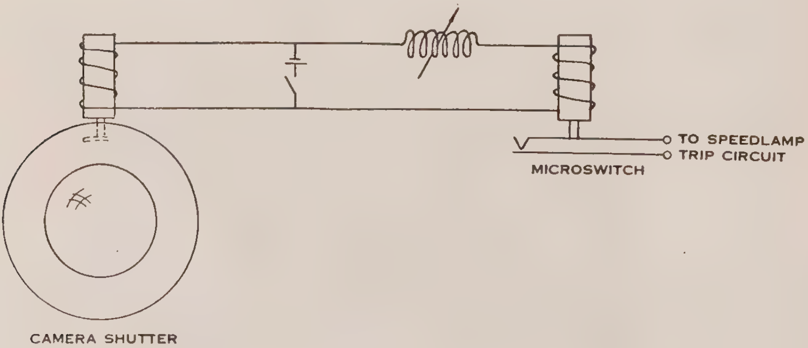


Fig. 196. Kodatron Synchro-Timer.

metal stand, an 18-inch reflector, and a flash tube on a telescoping steel support which can be raised to a height of 8 feet. The base is fitted with rubber-tired ball-bearing casters.

Since only a small fraction of a millisecond is required to complete the flash of the Kodatron Speedlamp it can be used effectively for stopping extremely fast motion. Pictures of ballet dancing, wrestling and boxing matches, and the like, result in critically sharp definition in all parts of the subject irrespective of the rapidity with which the action takes place. Speedlamp portraits possess a realism which can be achieved easily by posing the subject under room level illumination. When the desired pose is observed it is only necessary to flash the lamp to instantly record this pose on the film.

Under low illumination levels pictures can be taken using the open flash technique of opening the shutter, flashing the lamp and then closing the shutter. However, where the general room illumination is high enough to record a secondary image on the film it is necessary to synchronize the flash of the Speedlamp with the shutter, and use a high enough shutter speed to prevent sufficient secondary image forming light from reaching the film. In other words, the flash from the Speedlamp must produce the entire image on the film if the motion stopping ability of the flash is to be secured.



WIRING DIAGRAM for KODATRON SYNCHRO-TIMER
FIG 5-34

FIG. 197. Wiring Diagram for Kodatron Synchro-Timer.

The flash from the Speedlamp is completed in less than one millisecond after the trip circuit is closed. The time to full shutter opening for most manually set shutters is approximately 5 milliseconds. Therefore, for a device to synchronize the flash from this lamp with the action of the shutter it must perform the reverse function of a synchronizer intended for use with flash lamps; namely, it must delay the closing of the lamp circuit until the shutter has opened fully. The Kodatron Synchro-Timer, shown in Fig. 196, was designed to accomplish this. Fig. 197 shows the wiring diagram for this timer which consists of two matched solenoids connected in parallel across a suitable battery. One solenoid serves to trip the camera shutter while the other actuates a micro-switch which in turn closes the Speedlamp trip circuit. A variable inductance, wired in series with the micro-switch solenoid, delays its action until after the shutter solenoid has tripped the shutter. The length of this delay can be controlled by adjustment of the variable inductance so that the Speedlamp is flashed at the instant the shutter blades reach the full open position.

CHAPTER VI

PHOTOCHEMISTRY

Photochemistry.—The study of the chemical changes produced by radiation is known as photochemistry. The term radiation includes all forms of radiant energy as: visible light, ultra-violet, x-rays, gamma rays, infra-red, electric and cosmic rays. Chemical changes, or reactions, are caused by molecules or atoms that have become activated. According to the principles of chemical kinetics, molecules, or atoms, are activated when they absorb energy due to collisions with other molecules and atoms, or when they absorb radiant energy, such as light, from an external source. Only the radiation having the proper frequency and energy to be absorbed can effect a chemical change.

The types of radiation are differentiated from each other by differences in wave length. Wave lengths are commonly expressed in millimicrons, mμ, or Angstrom Units (Å).

$$\begin{aligned} 1\ \mathrm{m}\mu &= 1 \text{ millionth of 1 millimeter,} \\ 1\ \mathrm{A} &= 1/10 \text{ millionth of 1 mm.} \end{aligned}$$

or

$$\begin{aligned} 1\ \mathrm{m}\mu &= 10^{-6}\ \mathrm{mm.} = 10^{-7}\ \mathrm{cm.}, \\ 1\ \text{Å} &= 10^{-8}\ \mathrm{cm.}, \end{aligned}$$

$$1\mathrm{m}\mu = 10\ \text{Å}.$$

Since the velocity of light is constant, 3×10^{10} cm. per second, the frequency of vibration can be calculated from

$$\lambda\nu = c,$$

$$\nu = \frac{c}{\lambda},$$

where c = velocity of light and λ (lambda) = the wave length in centimeters per second, and ν (nu) is the frequency of light.

Quanta.—While radiation is propagated in a form of wave motion, Planck showed, in 1901, that radiant energy is emitted, or absorbed discretely in small particles or units of energy called quanta. The quantum theory states that radiation is discontinuous and that certain restrictions apply when this energy is transferred to molecules or electrons. The energy of the quantum varies with the frequency of the radiation:

$$\epsilon = h\nu,$$

where ϵ (epsilon) is the energy of the quantum, h is Planck's constant equal to 6.547×10^{-27} erg. sec., and ν (nu) is the vibration frequency. From this it will be seen that as the wave length of the radiation decreases, the frequency becomes greater, and the energy of the quantum becomes larger.

QUANTUM ENERGY FOR DIFFERENT RADIATIONS

Radiation	*Wave length*	*Frequency*	*Quantum Energy*
X-ray	1 Å	3×10^{18}	1.96×10^{-8} ergs
Ultraviolet	1,000	3×10^{16}	1.96×10^{-11} "
Visible, violet	4,000	7.5×10^{14}	4.91×10^{-12} "
Infra-red, short	10,000	3.5×10^{14}	1.96×10^{-12} "

Einstein has shown that light quanta not only carry energy but have a mass which varies in proportion to the energy, according to the relativity equation:

$$m = \frac{h\nu}{c^2},$$

where c is the velocity of light.

The quantum theory has been particularly successful in explaining the photoelectric effect, black-body radiation, x-ray emission, and the discontinuous series of spectra.

The Photoelectric Effect.—In 1905 Einstein extended Planck's ideas and proposed that heat and light were composed of quanta. The quantum of light then became a corpuscle of light, now better known as the photon. By the use of this assumption, instead of the classical wave theory Einstein was able to overcome certain difficulties in explaining the photoelectric effect.

Einstein predicted that when the surface of the metal is exposed to light, the energy of the quantum is used to expel electrons from atoms of the metal. The kinetic energy of the expelled electron is equal to:

$$\tfrac{1}{2} mv^2 = h\nu - w,$$

where m and v are the mass and velocity of the photo-electron, $h\nu$ is the

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PLANCK—Ann. Physik **4** (1901) 553.

energy of the quantum and w is energy required to remove the electron from the atom or metal surface, i.e., work function.

$$\tfrac{1}{2}mv^2 = h\nu - h\nu_0, \quad w = h\nu_0.$$

By connecting a positive potential to the surface of the metal, Millikan was able, 1916, to measure the potential which is just sufficient to stop the ejection of electrons. The force of attraction is then equal to the kinetic energy of the electrons.

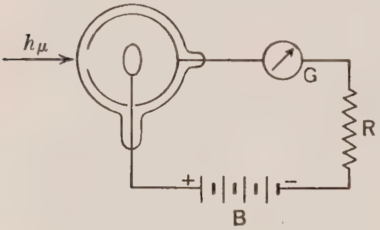

FIG. 198. Diagram of Photoelectric Cell.

$$Ve = \tfrac{1}{2}mv^2$$

or

$$\tfrac{1}{2}mv^2 = Ve = h\nu - w.$$

In this formula V is the potential difference in electrostatic units, e is the charge of the electron in electrostatic units (4.77×10^{-10}), $h\nu$ is the energy of incident radiation and w is the energy required to bring the electron to the surface of the metal. On the basis of the above equation, the energy and velocity of the ejected electron is proportional to the frequency of light. The number of photoelectrons emitted varies directly as the light intensity.

Electron velocities are often expressed in terms of volts. The electron-volt is defined as the energy of an electron that has fallen through a potential difference of one volt.

ENERGY OF PHOTON

Electric lamp	2	electron-volts
X-rays	$2 \times 10^4 - 1 \times 10^5$	" "
Gamma rays	2.5×10^6	" "

Spectra.—Newton showed in 1776 that white light was a mixture of colors by passing a beam through a prism. Light of shorter wave lengths, as violet, was refracted more than light of the longer wave lengths, as red.

In 1858 Bunsen and Kirchoff designed the first practical spectroscope. By use of this instrument the spectra of the various elements could

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EINSTEIN—Ann. Physik **17** (1905) 1932; **20** (1906) 199.
MILLIKAN—Phys. Rev. **7** (1916) 362.
HUGHES—Bull. Nat. Res. Council 2, Part 2, April (1921).
MILLIKAN—The Electron, University of Chicago Press (1924).

be examined. Two types of spectra were observed: line spectra and band spectra. Line spectra are produced by the activation of atoms and molecules in a vapor or gas. Gases may be activated to luminescence by means of discharge tubes. Metals are partially vaporized when used as electrodes for spark and arc discharges. Compounds can be heated in a flame or placed in cored electrodes. Band spectra may be considered as a series of lines very close together.

Line spectra are of two kinds: Adsorption spectra—produced by passing light from a continuous spectrum through a body of gas. Frequencies capable of being absorbed by the electrons in atoms will be observed as dark lines which are characteristic for each element. These lines are similar to the Fraunhofer lines in the solar spectrum. Emission spectra are observed as bright lines when an element radiates light. The bright lines occupy the same positions as do the dark lines in the adsorption spectrum. However, emission spectra always contain more lines than adsorption spectra.

Balmer Series of Hydrogen Spectra.—In 1885, Balmer found that wave lengths for the visible spectrum of hydrogen could be expressed by the formula:

$$\lambda = 3645 \frac{n^2}{(n^2 - 4)}$$

where λ is in Angstroms and n is a whole number equal to or greater than 3, i.e.:

$n = 3$ $\lambda = 6560$ A $H\alpha$ line red,
$n = 4$ $\lambda = 4860$ A $H\beta$ line blue.

Soon afterward Rydberg found it more convenient to represent the lines of the Balmer series in terms of frequency rather than in wave lengths.

$$\nu = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right).$$

The above formula represents the Rydberg equation in which the frequencies of the successive lines of the Balmer series are obtained when $n_1 = 2$ and n_2 is 3, 4, 5, 6, etc. R is the Rydberg constant which has a frequency value equal to 3.291×10^{15} vibrations a second.

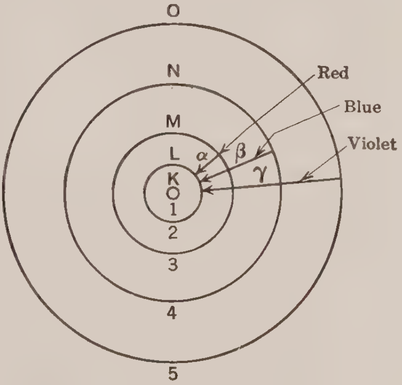

FIG. 199. Emission Spectrum of Hydrogen Balmer Series.

Since this equation gave large numbers, Ritz suggested the use of wave numbers instead of frequency.

$$\nu = \frac{c}{\lambda};$$

$$\text{therefore } \nu \text{ is proportional to } \frac{1}{\lambda};$$

$$\text{then} \qquad \nu^1 = \frac{1}{\lambda},$$

where ν^1 is the number of waves per second, or wave number. The new formula is known as the Balmer-Ritz equation and is obtained:

$$\nu^1 = N\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right);$$

N is a constant equivalent to the Rydberg constant since $\nu = c\nu^1$ and has a value equal to 109,700 cm.$^{-1}$.

Following the discovery of the Balmer series, five other series of hydrogen spectra have been found. The position of the various lines may be calculated by means of the Rydberg formula.

Series	n_1	n_2	*Region*
Lyman	1	2, 3, 4, 5, 6	ultra-violet
Balmer	2	3, 4, 5, 6	visible
Paschen	3	4, 5, 6	infra-red
Brackett	4	5, 6	far infra-red
Pfund	5	6	far infra-red

X-ray Spectra.—Barkla, 1911,[1] studying the scattering of x-rays, found that each element irradiated with x-rays emits both hard and soft x-rays which are characteristic of the element. The hard rays were designated by the letter K and the soft rays by the letter L The characteristic L rays consist of lines in a second spectrum and have wave lengths longer than those of the K spectrum.

Having discovered that x-rays undergo reflections at crystal surfaces, W. L. and W. H. Bragg, in 1912, built the x-ray spectrometer.[2] With the aid of this instrument they were able to discover several orders of x-ray spectra.

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[1] Barkla, *Phil. Mag.* **21** (1911) 648.

[2] Bragg, *Phil. Mag.* **24** (1912) 1024; **27** (1914) 703.

Mosely, in 1913, succeeded in photographing characteristic x-ray spectra for a number of elements. He showed that the penetration of x-rays generated by targets of different metals is a linear function of the element when arranged in the order of increasing atomic weights. As the atomic number increased, the series of lines constituting the x-ray spectrum shifted toward the shorter wave lengths. Elements having high atomic numbers were found to have two additional series. The series were designated by the letters K, L, M.

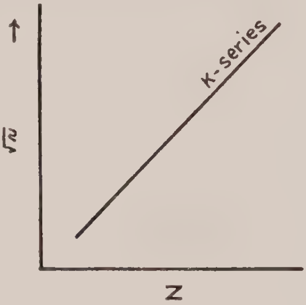

FIG. 200.

By plotting the square root of the frequency, as the α line of the K series, for the different elements against the atomic number, Mosely obtained a linear function which is represented by the following equation:

$$\sqrt{\nu} = a(Z - b).$$

in which Z is the atomic number and a and b are constants.[3]

Structure of Atom.—Based on studies in radioactivity dealing with the deflections of Alpha particles, Rutherford, 1911,[4] was the first to suggest the nuclear theory of atomic structure. The atom, according to this theory, is a miniature solar system in which a number of positive charges (protons) are packed closely together in a nucleus at the center of an atom. Surrounding the nucleus at various distances are a number of negative charges (electrons) which are equal in number to the positive charge in nucleus. Thus, an atom of an element having the atomic number Z has Z electrons each carrying a negative charge $-e$, and a nuclear charge, $+Ze$. The result of the whole represents a neutral atom.

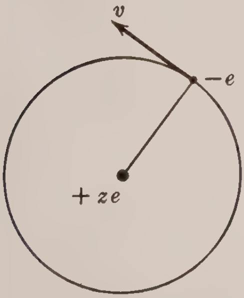

FIG. 201. Rutherford Model of Hydrogen Atom.

The Bohr Atom.—By making use of Einstein's photo-electric equation and Rutherford's atom as a model, Bohr was able, in 1913,[5] to extend the quantum theory to the interpretation of spectra obtained from hydrogen. With this theory he was able to derive the value of the Rydberg constant and the formula for the Balmer series of hydrogen.

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[3] Moseley, *Phil. Mag.* **26** (1913) 210; **27** (1914) 703.

[4] Rutherford, *Phil. Mag.* **21** (1911) 669.

[5] Bohr, *Phil. Mag.* **26** (1913) 1, 476, 857.

By rearranging the Einstein equation into the form

$$\nu = \frac{\frac{1}{2}mv^2 + w}{h}$$

and substituting frequency ν for wave number, ν^1 in the Ritz equation

$$\nu^1 = A - B.$$

Bohr showed that both equations could be written in the form

$$\nu = \frac{\text{Energy}}{h}$$

for $\frac{1}{2}$ mv is kinetic energy of the electron and W is the work function or energy required to bring the electron to the surface of a metal. Thus:

$$\nu = \left(\frac{W_2}{h}\right) - \left(\frac{W_1}{h}\right),$$

where W_2 and W_1 are energies. Then:

$$h\nu = W_2 - W_1.$$

According to Bohr's theory, the electrons of an atom may exist in different energy levels—E_1, $E_2 \cdots E_n$, without emitting or absorbing energy, but when an electron jumps from one level to another, E_2 to E_1, a quantum is absorbed or emitted and the energy of the atom changes from W_2 to W_1.

$$h\nu = W_2 - W_1$$

or

$$h\nu = E_2 - E_1.$$

Bohr assumed that the electron can revolve about the nucleus in any one of a set of particular orbits without radiating energy. Bohr further assumed that for an atom to be in a state of equilibrium, the centrifugal force must be equal to the force of electrostatic attraction between the nucleus and the electron,

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2}$$

and that the angular momentum of the electron in each orbit is a multiple, n, of $(h/2)\pi$,

$$mvr = \frac{n \cdot h}{2\pi}.$$

Then the energy, E_n, for any orbit, n, is

$$E_n = \frac{-2\pi^2 e^2 (Ze)^2 m}{n^2 h^2},$$

where m is the mass of the electron, e is the charge on the electron, Z is the atomic number, h is Planck's constant and n is a multiple.

When an electron jumps from one orbit to another, the energy of the quantum emitted is expressed by

$$hv = E_{n2} - E_{n1} = \frac{2\pi^2 m Z^2 e}{h^2}\left(\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right).$$

If wave number, v^1, is substituted for the frequency, v, then we obtain

$$v^1 = \frac{2\pi m Z^2 e^4}{ch}\left(\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right).$$

A constant equal to the value of the Rydberg constant, R, is obtained by grouping terms

$$R = \frac{2\pi^2 m e^4}{ch^3}.$$

In the case of hydrogen, the atomic number, $Z = 1$ and

$$v^1 = R_H\left(\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right),$$

where $R_H = 109{,}677.76$ cm.$^{-1}$.

By setting $n_1 = 2$ and making n_2 greater than 2, values are obtained which check closely with the observed lines in the Balmer series.

Since $v^1 = \frac{1}{\lambda}$ cm. and Å $= 1 \times 10^{-8}$ cm., then when

n_2	Å
3	6564.8
4	4862.7
5	4341.7
6	4102.9

Quantum Numbers.—While the Bohr theory accounted for the position of lines in the spectrum of atomic hydrogen, it did not account

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JAUNCEY—Modern Physics. 2d Ed. Van Nostrand (New York 1937).

for the fine structure of lines which are observed by spectroscopes with high resolving power.

To account for these lines various modifications of the Bohr theory have been made. Sommerfeld (1915) [6] suggested an atom in which electrons rotate around the nucleus in elliptical orbits. The momentum of the electrons can be resolved along the radius vector and angular momentum in accordance with radial and azimuthal quantum numbers. These numbers can be grouped and shown to be equal to the principal quantum number, *n*, of the Bohr theory. According to Sommerfeld's modification,[7] the azimuthal quantum number determines the ellipticity of the orbit. P. Epstein (1916) computed the perturbations in electron orbits and the change of energy in each due to the excitation of hydrogen and helium atoms in an electrostatic field, which is known as the Starke effect. P. Zeeman (1896) has shown that spectral lines are split into triplets when placed in a magnetic field. To explain this phenomena in terms of Bohr theory, it is necessary to assign a magnetic quantum number, *m*. Uhlenbech and Goudsmit (1925) showed [8] that many lines in the spectra are multiplets consisting of 2 or 3 lines close together. They explain the presence of multiplets in the spectum by assuming that an electron rotates or spins about its own axis and thus contributes to the total angular momentum. The spin is quantized according to the spin quantum number, *s*. Russell and Saunders [9] (1925) assume that the orbital angular momenta of the extra nuclear

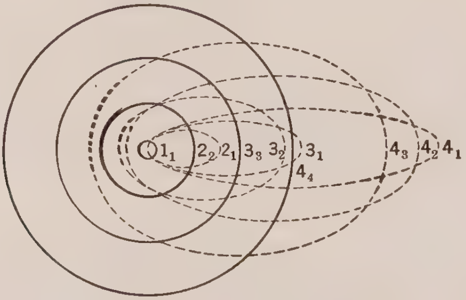

FIG. 202. Bohr-Sommerfeld Model of Hydrogen Atom Showing Stationary Orbits Corresponding to Principal and Azimutal Quantum Numbers.

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[6] A. Sommerfeld, *Ann. d Phys.* **III** (1916) 1. Paschen, *Ann. d. Phys.* **III** (1916) 901.

[7] P. Epstein, *Ann. d Phys.* **III** (1916) 489.

[8] Uhlenbeck and Goudsmit, *Nature* **117** (1926) 264.

[9] Russell and Saunders, *Astrophs. J.* **61** (1925) 38.

electrons of the atom are coupled together to give a total represented by the resultant quantum number, L. In addition there are several types of spectra which are known according to their appearance as: $s =$ sharp; $p =$ principal; $d =$ diffuse; $f =$ fundamental.

Pauli, in 1925, made a study of spectra and stated what is known as the Pauli exclusion principle.[10] According to this statement no two electrons in the same atom can have all four of their quantum numbers identical. In other words, there can be only one kind of atom for each combination of electronic quantum numbers. The four quantum numbers used to describe the state of electron in the atom are:

$n =$ the principal quantum number,

where $n = 1, 2, 3, 4, 5$, the electrons are referred to as K, L, M, N, O, electrons, and are said to be in the K, L, M, N, O, shells respectively outside of the nucleus.

$l =$ orbital quantum number.

For each principal quantum number there are n sub-levels designated by the quantum number, l, whose values must always be one less than the principal quantum number, n. Electrons represented by $l = 0, 1, 2, 3$, are called the s, p, d, f, electrons and give rise to the sharp, principal, diffuse and fundamental series of spectra.

$m_l =$ magnetic quantum number.

m is dependent on l and can have values from $+1$ to -1, and 0. The magnetic quantum number accounts for the splitting up of spectral lines into components when the emitting source is placed in a magnetic field, a phenomenon known as the Zeeman effect.

$m_s =$ the electron spin number,
s can have values of $+\frac{1}{2}$ or $-\frac{1}{2}$

as the rotation is superimposed on the orbital motion.

The energy of an electron in any level is a function of n, l, m_l, and m_s. The effect of the last three terms is small in comparison with n, the principal quantum number.

Atomic Structure.—Since the spectra of electrons are represented by four quantum numbers and the rules governing their restrictions, it can be shown that the energy of every electron in the atom is different from that of all others. The number of electrons in any shell is limized by the possible arrangements of quantum numbers. Then, for the K shell: $n=1$; $l=0$; $m_l=0$; $m_s=\pm\frac{1}{2}$. Hence, since there are only two possible combinations, there can be only two electrons in the K shell. This shell accounts for the hydrogen and helium atoms.

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[10] Pauli, *Z. Physik* **31** (1925) 765.

For the L shell:

$$n = 2; l = 0, 1; m_l = 1, 0, + 1 \text{ and } s = \pm\tfrac{1}{2}.$$

With these combinations there are 8 possible arrangements in the L shell and the l shell can contain 8 electrons. This shell accounts for the elements of boron, carbon, nitrogen, phosphorus, oxygen, fluorine, and neon.

COMBINATIONS OF ELECTRONIC QUANTUM NUMBERS FOR *K* AND *L* SHELLS

	n (*Principal*)	l (*Orbital*)	m_l (*Magnetic*)	m_s (*Spin*)	*Total Combinations*
K Shell	1	0	0	$+\frac{1}{2}$	2
	1	0	0	$-\frac{1}{2}$	
L Shell	2	0	0	$+\frac{1}{2}$	8
	2	0	0	$-\frac{1}{2}$	
	2	1	-1	$+\frac{1}{2}$	
	2	1	-1	$-\frac{1}{2}$	
	2	1	0	$+\frac{1}{2}$	
	2	1	0	$-\frac{1}{2}$	
	2	1	1	$+\frac{1}{2}$	
	2	1	1	$-\frac{1}{2}$	

The total number of electrons in any shell is given by the formula $e=2N^2$ or $2(1^2+2^2+3^2+\cdots N^2)$ in which the values of the succeeding terms are 2, 8, 18, 32. These represent the number of electrons in the K, L, M, N, O shells and are equal to the number of elements in the periodic system.

Quantum Mechanics.—The restrictions of the quantum theory, based on laboratory measurements, have been studied by various workers. In 1924 de Broglie extended the dual nature of light to matter.[11] He assumed that a particle of mass, m, moving with a velocity, v, has associated with it de Broglie waves, whose wave lengths are given by the expression

$$\lambda = \frac{h}{mv}.$$

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[11] de Broglie, *Phil. Mag.* **47** (1924) 446.

Heisenberg and Born[12] have devised a theory for the foundation of the restrictions based on matrix calculus.

Schrodinger made use of de Broglie's ideas and developed a theory based on the application of differential equations to waves, a theory, that is known as wave mechanics. From both theories the restrictions of the quantum came out automatically as mathematical necessities. Both theories are included in what is now known as quantum mechanics. In 1927 Davisson and Germer[13] showed that electrons act like light and that streams of electrons have properties attributed to waves. Busch pointed out the analogy between electron paths and light rays and showed that the behavior of both in an electric field is identical, a discovery which paved the way for the electron microscope.

Band Spectra.—The idea of the quantum theory has been extended to the molecule and atoms in a molecule. It has been shown that a molecule can exist in a number of energy levels and that a change from one state to another results in the absorption or emission of energy which results in the production of a line in the spectrum having a definite frequency. In order to account for structure of band spectra, it is necessary to assume that the electronic, vibrational and rotational energies of molecules are quantized.

The emission of energy, due to the rotation of molecules, gives rise to spectra in the far infra-red. Energy emitted, due to the displacement of atoms within the molecule, produces vibration spectra and when these are superimposed on the rotation spectra, bands appear in the near (short) infra-red.

Collisions between Photons and Molecules.—Photochemistry has been defined as a study of chemical changes produced by radiation. Chemical changes, or reactions, are caused by molecules and atoms which have become activated by the absorption of energy due to collisions or radiation. Molecules activated by radiation absorb quanta. The energy of the quanta, or photon, varies with the frequency. Light of long wave lengths, low frequency, has less energy than light of short wave lengths, high frequency.

When a photon strikes a molecule, several results are possible: (1) no reaction, the photon did not have the proper energy to be absorbed,

[12] Heisenberg, *Z. Physik* **38** (1926) 411; **41** (1927) 239.

[13] Davisson and Germer, *J. Chem. Ed.* **5** (1928) 1041, 1255.

DUSHMAN—The Elements of Quantum Mechanics.

For discussion of the wave mechanics equation see GLASSTONE—Textbook of Physical Chemistry. Van Nostrand (1940) p. 74.

displacement of atoms in molecules and a photon of different frequency —(2) Raman effect; the production of high speed electron and a photon of lower frequency—(3) Compton effect; the disassociation of molecule into atoms, one of which becomes excited; the splitting off of an electron with the formation of a positive ion and the activation, or excitation, of the molecule. Molecules are activated in different ways depending upon the frequency of the absorbed radiation. The energies required for most chemical reactions range from 20,000 to 100,000 calories. Since visible and ultra-violet light have the shortest wave lengths, hence the greatest frequency and energy, these are most effective in producing chemical reactions.

Radiation	Å	*Calories per Molecule*	*Effect on Molecule*
Far infra-red. . .	$2 \times 10^5 -$	. . . .– 1400	rotation of molecule
Near infra-red. .	$8 \times 10^5 - 4 \times 10^3$	1400– 3500	displacement of atoms in molecule
Visible	$8 \times 10^3 - 4 \times 10^3$	3500– 71000	displacement of electrons in *outer* orbit of atoms
Ultra-violet. . . .	$4 \times 10^3 - 2 \times 10^3$	71000–142000	

Distribution of Energy.—When light falls on a substance, a part of the light is reflected, a part absorbed and the remainder transmitted. The energy relations may then be expressed as

$$E = R + A + T,$$

where E is the incident energy, R — the energy reflected, A — energy absorbed, and T — energy transmitted.

In Photochemistry it is necessary to take into consideration the amount of light distributed between the three divisions. Fresnel's law gives the relation between incident and reflected light. It is expressed by the equation:

$$\left(\frac{n-1}{n+1}\right)^2 I_0 = RI_0,$$

in which I_0 is the incident light, n is the refractive index of the medium for light of a definite wave length.

In solutions the amount of light absorbed depends not only on the thickness but also on the concentration. For like solutions of uniform thickness, the absorption of light in different concentrations is an exponential function of the concentration.

$$I = I_0 l^{-kmx},$$

where I_0 is the intensity of light striking the absorbing medium, I is the intensity light which has passed through a thickness, x, having the concentration of m, and k is a constant known as the molecular absorption coefficient; k varies with the nature of the dissolved material and with wave length.

Photochemical Laws.—In 1818 Grotthus stated the first law of photochemistry;—only the radiation which is absorbed can produce a chemical change. This law was re-stated by Draper in 1839 and has since become known as the Grotthus-Draper law. Although photochemical reactions are caused by the absorption of light, it does not follow that all radiation which is absorbed will produce chemical change. Much of the energy is converted into heat, while some may be emitted as light with a different frequency—giving rise to such phenomena as fluorescence and phosphorescence. The term radiation includes all electromagnetic vibrations from short gamma and x-rays to the long infra-red rays. Ultra-violet and visible radiation are most effective in producing photochemical changes. According to modern theories, the absorption of ultra-violet and visible light produces displacement of outer electrons in molecules or atoms causing the molecules to decompose or to react with other molecules. In cases where conditions are not suitable for reaction, the activated molecules emit their energy as radiation of a different wave length, or they may produce violent collisions with other molecules and thus dissipate their energy as heat. Some reactions are sensitive to a wide range of wave lengths, while others are affected by monochromatic light of definite wave length or by a narrow band of wave lengths. Einstein's law of photochemical equivalence states that in primary processes the absorption of one quantum is required for each molecule activated. As the energy of the quantum is equal to

$$\epsilon = h\nu$$

and since gram-molecule contains 6.06×10^{23} molecules, a number known as Avogadro's number, N, then to activate the molecular weight of any substance, the number of quanta required will be

$$U = Nh\nu = 6.06 \times 10^{23} \times 6.547 \times 10^{-27}\nu,$$

where ν is the frequency, h is Planck's constant. The number of quanta U is called the "Einstein."

The relation of one quanta per molecule activated holds for ideal conditions, as rarified gases having reversible monomolecular reactions and a narrow monochromatic absorption band. In most cases the reactions are not simple, but are often followed by a series of secondary or chain reactions. The number of molecules activated by the absorption of a quantum may vary from a fraction to several hundred. The ratio of the number of molecules that have reacted to the number of quanta absorbed, is known as quantum yield, Φ.

$$\Phi = \frac{\text{no. of molecules decomposed}}{\text{no. of quanta absorbed}} .$$

Types and Nature of Photochemical Reactions.—Various kinds of reactions are caused by exposure to light; among the types that have been studied are: synthesis, decomposition, oxidation-reduction, hydrolysis, halogenation, polymerization, allotropic change and ultramolecular rearrangement.[14]

Photochemical reactions differ from thermal reactions in that the former take place in the presence of light at normal or low temperatures. The intensity of light and size of container affect the rate of reaction. Photochemical reactions are often accompanied by dark or thermal reactions in opposite directions as

$$A \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} B.$$

Photochemical reactions may produce catalysts which in turn cause a thermal reaction. Some reactions have an induction period during which enough catalyst is produced to cause the reaction to proceed with normal speed. Other photochemical reactions continue after the illumination is stopped and exhibit after effects of a thermal nature. While thermal reactions are dependent upon concentration of reacting substances, photochemical reactions are often independent of the concentration. The energy available in photochemical reactions is greater than that of thermal reactions. This accounts for the fact that photochemical reactions are different from thermal reactions and are usually more complex.

Solid and Semi-solid Systems.—Most of the reactions studied in photochemistry have been in the field of gaseous systems. Little

[14] Sheppard, *Photography as a Scientific Instrument*, Blackie (1923) p. 113.

Einstein—Ann. Physik (4) **37** (1912) 832.

work has been done with liquid and solid systems. Of the solids sensitive to light only a few have been thoroughly investigated. Of these, only the decomposition of silver halides is of interest to photography.[15]

If certain substances, as gelatin, silver nitrate, halides of potassium and ammonium, are added to silver halides, these become more light sensitive. Materials of this type act as light catalysts and are known as "sensitizers." The presence of small quantities of sulfur bodies [16] (as "allyl isothiocyanate") in gelatin greatly increases the sensitivity of photographic emulsions. It is also known that the sensitivity of photographic emulsion is dependent on the size range of silver halide grains. Eggert and Noddack have studied [17] the light absorption processes of silver halides and found that they decompose into silver and halogen. The reaction has a quantum efficiency of one.

$$AgBr + h\nu = Ag + Br.$$

Light Sensitive Materials for Photography.—Of the many light sensitive systems only a few have found commercial applications in photography. Sheppard lists the following: (1) silver halides and salts that produce silver images; (2) iron complexes which produce ferrous salts. These may be converted into platinum, palladium or prussian blue images; (3) alkaline dichromates with colloids that produce chromium oxides which are capable of tanning gelatin; (4) Diazo compounds that lose nitrogen and are decomposed into products which may be coupled to form a dye; (5) sensitive dyes that are bleached by light.[18]

Silver Processes.—If silver halides, as silver chloride, silver bromide, and silver iodide, or silver salts, as silver nitrate, silver citrate, are placed in protective colloids, as gelatin, agar agar, albumen, casein, collodion or cellulose esters, suspensions are formed which, if coated on supports, as glass, film base or paper, are known as photographic emulsions. Of the silver salts, the silver halides are most important.

On exposure to light silver salts exhibit two types of photographic reactions, printing out—producing visible images—and the formation of latent images which may be developed into visible images. Visible

[15] Franck and Kohn, *Z. Physik* **44** (1927) 607.

[16] Sheppard and Punnett, U.S.P. 623,499.

[17] Eggert and Noddack, *Z. Physik.* **31** (1925) 922.

[18] Sheppard, *Ind. Eng. Chem.* **22** (1930) 555.

FRIEDMAN—Light Sensitive Systems. Amer. Phot. (1940) 294.

images are composed of colloidal silver adsorbed to or occluded in silver halide. By x-ray studies, Koch has shown that the first traces of a visual image is composed of metallic silver.[19] The latent image serves to catalyze the development process causing a reduction of silver halides. There are two basic theories as to the origin of the latent image. Renwick suggests that the colloidal silver acts as a negative sol and is coagulated by the action of light to form a neutral gel which may catalyze the reduction of silver halide. The second theory assumes that on exposure the halogen ion loses an electron which is adsorbed by a silver ion forming a metallic speck.[20]

$$\begin{aligned} Br^- + h\nu &\rightarrow Br + e, \\ Ag^+ + e &\rightarrow Ag, \\ Br + Br &\rightarrow Br_2. \end{aligned}$$

It is thought that silver halide crystals have crystal lattices in which the silver and bromine exist as ions. On exposure the ions undergo changes given in the equations above. The silver formed acts as nucleus, or center, for development of the silver halide grain.

The exposure of photographic emulsions produces latent images which can be developed when the image is treated with a selective reducing, or developing agent, in solution. Latent images are not visible to the eyes, but when treated with reducing agents the products of the photochemical reaction act as a catalyzer which, in turn, causes reduction of the surrounding silver molecules. The quantum yield for reaction of this type may be as great as 300. The exact mechanisms for the processes of latent image formation are still uncertain. A discussion of the various theories will be found in Chapter IX.

Quanta Required for Latent Image Formation.—The application of the quantum theory to photographic exposures and latent image formation has been the subject of study for many investigators. Silverstein studied the quantum theory of photographic exposure. James, James and Coleman, and Webb[21] have investigated theoretically the number of quanta required to form the photographic latent image.

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[19] Koch and Vogler, *Ann. Physik* **77** (1925) 495.

[20] Fajans, *Chem. Ztg.* **45** (1921) 666. Toy and Edgerton, *Phil. Mag.* **48** (1924) 947. Spencer, *Proc. 7th International Cong. Phot.* (1928) 358.

[21] For a good bibliography of work up to 1939 consult paper by Webb in *J. Opt. Soc. Amer.* **29** (1939) 309.

SHEPPARD—The Formation of the Photographic Latent Image, Phot. J. **68** (1928) 397.

Silverstein has determined mathematically the number of quanta needed for developability of a silver halide grain.

The question as to the number of quanta utilized in latent image formation is an important problem in photographic theory. One method of approach has been the mathematical analysis of the characteristic H and D curves for an emulsion.[22] A fundamental assumption of the theoretical investigations is that a fixed minimum number of quanta are required to produce a latent image that is just developable. This minimum number is assumed to be the same for every grain. Analyses of this assumption have led to the conclusion that a small number of quanta, 1 to 4, are involved in latent image formation. Contrary to this Webb has shown that theoretical curves based on a wide variation of sensitivity among grains, 1 to 1000, are also in agreement with experimental H and D curves. Webb and Evans [23] using the method of intermittent exposures found that some grains require more than 64 quanta to become developable. Since 2 or 3 electrons may be placed on a speck without causing neutralization, the number of quanta required for latent image formation for some grains must be greater than 100. Although a few grains may require 1000 or more quanta, such are scarce. Eggert and Noddack state [24] that the number of quanta falling on a grain may be as high as several hundred.

By applying a method of graphic analysis to photographic exposure and assuming that the sensitivity variation among grains of a photo-

[22] Silverstein, *J. Opt. Soc. Amer.* **31** (1941) 343.

[23] Webb, *J. Opt. Soc. Amer.* **31** (1941) 348. Webb and Evans, *J. Opt. Soc. Amer.* **41** (1941) 355.

[24] Eggert and Noddack, *Z. Physik* **20** (1923) 299.

Silberstein—Quantum Theory of Photographic Exposure. Phil. Mag. **44** (1922) 257; **44** (1922) 956; **45** (1923) 1062; **5** (1928) 464; Proc. Int. Math. Congress, Toronto (1924) p. 127.

James and Coleman—Quantum Theory of the Latent Photographic Image. J. Chem. Phys. **2** (1934) 483.

James—Quantum Theory of Latent Photographic Image. **2** (1934) 132.

Webb—The Number of Quanta Required to Form the Photographic Latent Image as Determined from Mathematical Analysis of the H and D Curve. J. Opt. Soc. Amer. **29** (1939) 309; **31** (1941) 348, 559.

Silberstein—On the Number of Quanta Required for Developability of a Silver Halide Grain. J. Opt. Soc. Amer. **31** (1941) 343.

Selwyn—Number of Quanta Required to Form the Photographic Latent Image as Determined from Mathematical Analysis of the H and D Curve. J. Opt. Soc. Amer. **29** (1939) 518.

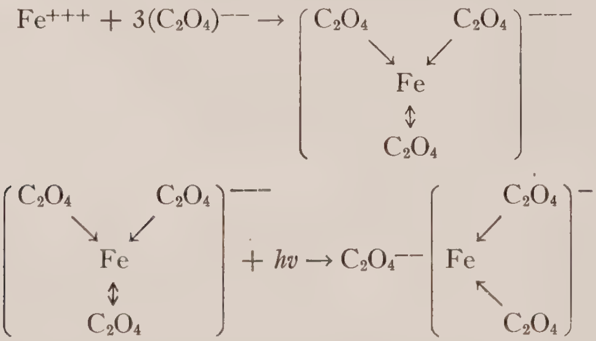
Toy—Phil. Mag. **44** (1922) 364.

graphic emulsion depends on the inherent variation in grain sensitivity among grains of the same size class as well as upon size distribution, Webb was able to derive theoretical equations [25] for H and D curves in agreement with experimental data obtained by Wightman, Trivelli and Sheppard [26] for the exposure grain-count of an actual emulsion.

The number of quanta required for latent image formation does not necessarily agree with the number of silver atoms in the latent image. This difference may be due to the fact that the energy of quanta may not be sufficient to cause the formation of silver atoms, silver atoms formed may evaporate, or they may be lost by the speck.

According to Mott,[27] quanta adsorbed by a crystal may undergo three fates, the energy may be converted into heat, re-emitted as fluorescence, or used in the production of photo-electric energy.

Iron Processes.—Ferric salts in the presence of organic acids form complexes which on exposure to light are reduced to ferrous salts.



This reaction forms the basis of the blue-print process and platinotype.

Bichromate Processes.—The second most important photographic process depends upon the action of light on bichromated colloids. The investigations of Eder, Lumiere and Seyewetz, Bowen [28] and others show that the bichromate is decomposed to Cr_2O_3 which in turn reacts with the acid bichromate ion $(HCr_2O_7)^-$ to form a complex which is responsible for the tanning of the colloid. Colloids hardened in this manner are utilized in various photo-mechanical processes and in imbibition and pigment printing processes such as carbon, carbro, gum-bichromate and bromoil.

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[25] Webb, *J. Opt. Soc. Amer.* **29** (1939) 314.

[26] Wightman, Trivelli and Sheppard, *J. Phys. Chem.* **28** (1924) 529.

[27] Mott, *Proc. Roy. Soc.* **167A** (1938) 384.

[28] Bowen and Yarnold, *J. Chem. Soc.* (1929) 1648.

ALLMAN AND WEBB—J. Chem. Soc. (1929) 1531.

Other Metallic Salt Processes.—Various compounds of Uranium, Mercury, Thallium, Platinum, Cobalt, Nickel, Cerium, Molybdenum and Tungsten show light sensitiveness. Of these the most important for photographic use are: Uranium, Mercury, Thallium and Platinum. At present, no printing emulsions employing these salts are available, commercially.

Dye Processes.—With the exception of bleach-out, diazo and silver-dye bleaching processes, photography has not made much use of reactions common to organic chemistry.

Many dyes are sensitive to light, either changing in color or more frequently bleaching out to colorless or nearly colorless substances. The exposure required for bleaching varies widely with different dyes. The exposure required for bleaching of some dyes is greatly reduced, if other substances, termed sensitizers, are present. Dyes are usually sensitive to the shorter wave lengths of light, chiefly to ultra violet. Dyes sensitive to light are generally bleached by light of a complementary color. Dye bleaching may be either a process of oxidation, reduction, decomposition or internal rearrangement.

Bleach-out and silver-dye bleach processes are employed in printing mediums for color photography, while the diazo process is widely used in plan copying papers.

a. The Bleach-out Process. The bleach-out process, also known as dye bleaching, utilizes the sensitivity of dyes for bleaching action and forms images composed of dyes. The dyes in the dye layer are bleached in proportion to exposure (light action). The image may be positive or negative. The bleach-out process is usually employed to make positives from positives.

Dye bleaching, as a photographic process, was first recognized by Liesegang in 1889.[29] The work of Vallot, Neuhaus, Worel, Szczepanik, Smith and Limmer was ably summarized by the latter in 1911.[30] More recently the reactions involved have been studied by Koenig, Steigman,

[29] Liesegang, *Phot. Arch. No.* 633 (1889) 328.

[30] Limmer, Das Ausbleichverfahren, Halle (1911).

FRIEDMAN—Uranium Printing. Am. Phot. **33** (1939) 846.

PLOTNIKOW—Allgemeine Photo Chemie, Walter de Gruyter, Leipsig (1936).

Eder Handbuch IV, 4 (1929).

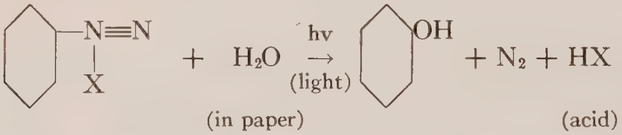
Mudrovcic,[31] Kogel,[32] Lasreff[33] and Wendt.[34] While the action of sensitizing agents on dyes of oxazine, thiazine, azine, phthalein, triphenyl-methane and xanthonium classes have been studied, only basic dyes of the xanthene group sensitized with thiourea derivatives and acid dyes used with activating and sensitizing agents are employed for the production of images. Fixation is accomplished by treating with agents like sulfurous acid which destroy sensitivity of the dye. Some xanthonium dyes found suitable for dye bleaching are:

Capri Blue GON
Flavendule
Methylene Blue
Pyronine G
Rosindule 2B
Rhodamium S

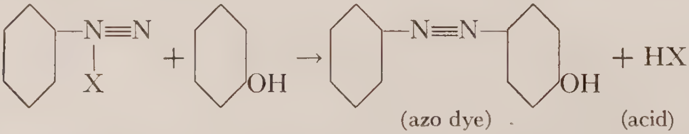
b. The Diazo Process. The bleaching of dyes finds its most important application in photography in the plan copying papers of which Ozalid, Océ and Primuline are examples.

In the diazo process, exposure causes diazonium salts, which are dye intermediates, to undergo chemical changes which affect their capacity to form dyes, i.e.:

1. Exposure of the diazonium salt causes the destruction of the diazonium linkage.



The residual diazonium salt, unexposed portion, may couple to form an azo dye.



As coupling takes place in an alkaline medium only, it is necessary to neutralize the acid, i.e., ammonia vapors

$$HX + NH_3 \rightarrow NH_4X$$

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[31] Mudrovcic, *Phot. 2nd* **27** (1929) 1313.
[32] Kogel, *Phot. Korr.* (1926) 9, 15.
[33] Lasreff, *Zeit. Phys. Chem.* **78** (1912) 657.
[34] U.S.P. 1,850,162, 1,871,830, 1,880,573, 2,049,005.

FRIEDMAN—Bleach-out Process. Am. Phot. **32** (1938) 821.
Progress in Color. Brit. J. Phot. **87** (1940) 419.

With this method a dark colored line positive is obtained from a positive original.[35]

2. On exposure to light the diazonium salt may undergo an internal rearrangement so that only one form of the salt will couple. According to the materials used either a positive or negative image may be produced.

The discovery of the diazo reaction was made by Griess in 1858. West, using diazo salicylic acid and its derivatives, made the diazo pictures in 1885. The first practical process was introduced by Freer who discovered that diazo-sulfonates after exposure would couple to form dyes. This reaction yielded a negative image. Green, Cross and Bevan, 1890, discovered that diazotized primuline could not couple after exposure. Their method gave a positive image from the copy. In 1923, Kogel discovered the stable class of light sensitive compounds, the diazo-anhydrides, which gave rise to the first dry development papers. It was possible to incorporate these salts in gelatin solutions together with suitable couplers and organic acids and produce, after exposure and fuming with NH_3, coupled images in the unexposed regions.

c. Silver-Dye Bleach Process. The Silver-Dye Bleach Process (Dye Destruction) differs from the bleach-out process in that dyes are bleached by chemical means instead of by the action of light. The silver image may act as a catalyst or it may be made an agency for the destruction of dyes. The destruction of the dye may take place either at a point where the silver image is formed or in areas without a silver image, the effect varying in proportion to the silver density. In either case, the silver image determines the position of the dye image remaining after processing. A survey of dye destruction methods was made by Hymer in 1935.[36]

Dye destruction processes are grouped into two methods, depending on whether a silver image is used or not:

1. Dyes in the presence of the silver image may be destroyed by either oxidation, reduction, catalytic, or bleaching processes.

Dyes in the presence of silver images may be destroyed by oxidizing agents as hydrogen peroxide,[37] ammonium persulfate, potassium bro-

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[35] Spencer, *Proc. Seventh Int. Congress* (1928) 358.

[36] Hymer, *Sci. Pub. Agfa Central Lab.* **4** (1935) 177.

[37] Schingel, *Brit. J. Phot.* **52** (1905) 608.

SAUNDERS—The Aromatic Diazo Compounds, Arnold & Co., London (1936).
FRIEDMAN—Amer. Phot. **34** (1940) 142.

mate and lead chromate.[38] Reducing agents, like sodium hydrosulfite and stannous chloride,[39] destroy dyes while the silver image is developed. The silver image may also be converted to substances which are capable of destroying the dye either directly or indirectly. Vanadium ferrocyanide and chromic acid [40] is an example of this type. In other cases the silver image may be bleached with an acid solution of thiocarbamide,[41] or dyed with a dye that can be easily reduced to a leuco base.[42] The latter produces a reversed dye image when silver is removed. Two essentials necessary for these processes are the use of a silver halide solvent and an acid reaction.[43]

2. Dyes may be destroyed in areas that do not contain a silver image. In this case, dyes in the presence of silver halides are bleached. Typical bleaching reagents are: calcium hypochlorite and glacial acetic acid,[44] sodium bromate and sulfuric acid,[45] or iodic acid with sulfuric acid.

Dye destruction methods have been employed successfully in Gasparcolor. In this process the developed silver image is bleached with a silver solvent containing ferric salts. The silver salts are then converted to silver, and the dye in the emulsion is bleached by exposure and treatment with hydrosulfite and bromine solutions.

Among the dyes found suitable for such a process are: Diamine pure Blue FF, Bengo purpurine 10B, and Mordant Yellow G.D.

Because of slowness of materials employing dye destruction methods, they are not suitable for negative purposes. See chapter on integral tripacs for color materials employing dye destruction processes.

Quantum Yields for Photographic Reactions.—Reaction processes and quantum yields for four photographic systems have been summarized by Eggert.[46]

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[38] Schweitzer, Fr.P. 496,217 (1915).

[39] Christensen, *Jahrbuch* **29** (1915) 164; D.R.P. 327,591.

[40] Luther and Holleben, D.R.P. 369,485.

[41] Gaspar, *Zeit. Wiss. Phot.* **34**, 119.

[42] Crabtree, *Abridged Scientific Publications of Kodak Research Laboratories* **4** (1919–20) 198.

[43] Luppo-Cramer, Eder's Handbuch **2** (1927).

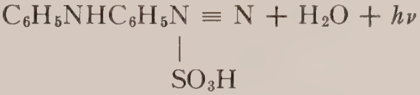
[44] Gaspar, *Brit. J. Phot. Colour Supplement* **27** (1933) 41.

[45] Schweitzer, B.P. 249,530.

[46] *Phot. J.* **76** (1936) 17.

The Photochemistry of the New Colour Film Processes. Die Photographische Industrie, 34, 46/47, Nov. 11/18, 1936; Brit. J. Phot. **84** (1937) 67.

Friedman—Gaspar Process. Am. Phot. **32** (1938) 130; **35** (1941) 855. Progress in Color. Brit. J. Phot. **87** (1940) 419, 433.

Sensitive Substance	Reaction Mechanism	Quantum Yield
Gelatino-silver chloride	$Cl^- + h\nu = Cl + \theta$ $\theta + Ag^+ = Ag$ $AgCl + h\nu = Ag + Cl$	$\phi = 1$
Gelatino-silver bromide	$Br^- + h\nu = Br + \theta$ $\theta + Ag^+ = Ag$ $AgBr + h\nu = Ag + Br$	$\phi = 1$
Diazo	 $C_6H_5NH\underset{\underset{SO_3H}{\vert}}{C_6H_5}N \equiv N + H_2O + h\nu$ $= N_2 + C_6H_5NH\cdot C_6H_5OH + H_2SO_4$	$\phi = 0.5$
Chromate-gelatine	$CrO_4'' + 3H$ (from gelatin) $+ h\nu = CrO\ 3OH'$ $CrO + gel \rightarrow$ Adsorption Product	$\phi = 0.5$

CHAPTER VII

THE PHOTOGRAPHIC EMULSION

Introduction.—A photographic emulsion is not a true emulsion but a suspension of a light-sensitive solid in a colloid. While light-sensitive emulsions may be prepared from the salts of several metals including mercury and thallium,[1] only those of silver halide are of practical importance. Albumin (1847) was the first colloid used in photographic emulsions; this was followed by collodion in 1851 which, in turn, was superseded by gelatin (1872). Although attempts have been made to use agar and casein, mainly in emulsions for printing papers, only gelatin is of practical importance.

In making an emulsion a solution of silver nitrate is added to a solution of gelatin containing an alkaline halide, the reaction in the case of silver bromide being $AgNO_3 + KBr = AgBr + KNO_3$. The gelatin is first allowed to swell in cold water and then dissolved by heat, after which the alkaline halide (either bromide, chloride or iodide) is added and finally silver nitrate.

The precipitation or "emulsification" of the silver halide in gelatin is a very critical operation; the particles must be of the proper size and evenly distributed throughout the gelatin solution. To increase the sensitivity, emulsions intended for use in the camera are subjected to a process known technically as ripening which is accomplished by heating the emulsion or by the addition of ammonia. After ripening, the emulsion is washed to remove the alkali nitrate (KNO_3) and other soluble substances.

Both of these operations are frequently omitted in the case of the less sensitive and more dilute emulsions employed for contact printing papers.

[1] Luppo-Cramer, *Die Grundlagen der Photographischen und Negativ-Verfahren.*

CARROLL—A Summary of Emulsion Knowledge. Brit. J. Phot. **79** (1932) 622, 637, 654, 684.

RENWICK—The Manufacture of Sensitive Emulsions as a Science and an Art. J. Soc. Chem. Ind. **42** (1923) 43.

THORNE-BAKER—Photographic Emulsion Technique. American Photographic Publishing Co., Boston 1941

The emulsions for films and plates intended for use in the camera consist of nearly pure silver bromide or silver bromide and a small amount of silver iodide, while the less sensitive emulsions used for papers consist of pure silver bromide (bromide papers) silver bromide and silver chloride (chloro-bromide papers) or silver chloride (developing out or gaslight papers) the order of sensitiveness decreasing generally in this order.

In negative emulsions, the silver halide forms from 30 to 40 per cent of the total weight of the dry emulsion. The proportion is usually much less in emulsions for printing papers.

While the formulas and manufacturing procedures employed in the preparation of commercial emulsions are closely guarded trade secrets, the general principles are well known and will be discussed in the following pages.

Gelatin.—If silver halide is formed in an aqueous solution by the double decomposition of a soluble halide, such as potassium bromide and silver nitrate, and the solution allowed to stand a short while, the silver halide will begin to precipitate upon the sides and bottom of the vessel. However, if the silver halide is formed in the presence of a colloid, such as gelatin, the solution, at first clear and slightly opalescent, becomes creamy or milky on standing and the silver halide does not precipitate out of solution but remains uniformly distributed in

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Charriou and Valette—Photographic Gelatin. Publ. Sci. Techn. Ministere de l'air, No. 124 (1938).

Fuchs—Testing Gelatins for Emulsions. Phot. Ind. **31** (1933) 254. Sci. et Ind. Phot. (II) **4** (1933) 160.

Sheppard—Effect of Concentration of Sensitizer on Speed, and Fog Corrections. Phot. J. **66** (1926) 399–409.

Sheppard—Sulphur Compounds and Photographic Emulsions. Sci. et Ind. Phot. (II) **7** (1936) 361.

Sheppard—Photographic Gelatine. Phot. J. **65** (1925) 380.

Sheppard, Elliott and Sweet—Photographic Properties of Gelatine. Physical Chemistry of the Photographic Process. (Published as Transactions of the Faraday Society.)

Sheppard—The Modern Chemistry of Gelatine. Brit. J. Phot. **69** (1922) 677, 695, 706, 710; J. Ind. and Eng. Chem. **14** (1922) 1023.

Sheppard—Gelatin I (Monographs on the Theory of Photography). D. Van Nostrand Co. 1923.

Slade—Colloid Chemistry in Photography (Bibliography). Brit. J. Phot. **67** (1920) 645.

Slater-Price—Gelatine. Phot. J. **62** (1922) 356.

the solution. The colloid (gelatin) thus acts as an emulsifying medium, or vehicle, holding the particles of silver halide in suspension.

As a vehicle, gelatin is immensely superior to any other colloid. Of primary importance from the standpoint of photographic emulsions is the easy reversibility of the transition from the hydrosol to the hydrogel at readily attainable temperatures. As a hydrosol, it renders possible the formation of a suspension of silver halide particles in a medium which can readily be spread on paper, film, or on glass plates, converted by chilling into a hydrogel, and upon drying forms a vehicle capable of holding the photosensitive silver halide permanently in position on the base and at the same time is of such a nature as to allow the free passage of the solutions in processing. Thus it is the properties of the hydrosol which are of importance in the preparation of the emulsion and those of the hydrogel which concern its behavior in use.

Aside from functioning as a vehicle, gelatin acts as a protective colloid. Silver halide formed by precipitation in an aqueous solution is immediately attacked and reduced to silver by a developer whether exposed to light or not. If, instead of water, the silver halide is formed in a solution of a colloid such as gelatin, the rate of reduction is greatly decreased, especially for silver halide which has not been exposed to light. The difference in the rate of reduction for exposed and unexposed silver halide, when precipitated in a colloid, renders development possible. Without the protective action afforded by a colloid all possibility of obtaining an image is eliminated as the silver halide, whether exposed or not, is immediately reduced by the developer.

The exact mechanism involved in the protective effect of a colloid is not clear. It is probably very similar to, if not identical with, the protective action observed in the case of gold and silver sols; however, in the case of photosensitive silver halide, there is the added difficulty of accounting for the difference in the rate of reduction for exposed and unexposed silver halide.[2] Apparently the chief function of a colloid in restraining reduction by developing agents is by retarding the deposition of silver either by raising the metastable limit by the exclusion of the nuclei or by hindering the coalescence of the silver amicrons.[3]

It has long been recognized that emulsions of higher sensitiveness may be prepared with gelatin than with any other colloid. Until only a few years ago it was a disputed point as to whether gelatin should be regarded as directly responsible or whether it acted merely as a passive medium which facilitated the production of large and more sensitive crystals.

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[2] Slater-Price, *Phot. J.* **65** (1925) 94; Zsigmondy, *Kolloidchemie* 1922; Freundlich, *Capillarchemie* 1909.

[3] Sheppard, *Phot. J.* **69** (1929) 330.

It is now know that both viewpoints are correct and that ordinary commercial gelatin contains products which materially affect the sensitivity of the silver halide crystal. These were isolated by Sheppard and his coworkers in the Kodak Research laboratories and found to be allyl-isothiocyanate (mustard oil) and related sulfur-carbon compounds. The isothiocyanates are converted by ammonia into water-soluble thiocarbamides from which silver sulfide is formed as the result of a reaction, the nature of which is not clear.

Many other substances have been found to act as sensitizers, but it is probable that in all cases the sensitizing action is due to the silver sulfide formed since allyl thiocarbamide does not act as a sensitizer except under conditions which result in the formation of sodium sulfide.

The formation of sodium sulfide is retarded by a low bromine-ion concentration or by acids; it is greatly accelerated by ammonia and alkalis generally.

Emulsions prepared with gelatin free of such sensitizing agents possess only moderate sensitiveness regardless of the manner of preparation. The addition of a small amount of any one of the sensitizing substances results in a marked increase in sensitivity which increases as the concentration of the sensitizer up to a point beyond which general fog is produced.[4]

The amount of the sensitizing substance necessary for optimum sensitiveness is very small; photographically active gelatin contains from 1 part in 300,000 to 1 part in 1,000,000 of the sensitizing substance sufficient to convert only a few molecules per 100,000 of silver bromide to silver sulfide.[5]

The mechanism involved in the increase in the sensitivity of the silver halide crystal by silver sulfide will be discussed later.

A gelatin, to be suitable for photographic purposes, must be free from mineral or other products which would cause decomposition, from organic sulfur and other reducing substances, as well as copper, lead, and iron. It must have a high viscosity, which must be retained when heated, a good jelly strength and setting power, and finally must be clear and free from color. These conditions are met only by the purest gelatin extracted at a relatively low temperature.[6]

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[4] Sheppard, *Phot. J.* **66** (1926) 399.

[5] Sheppard, *Phot. J.* **65** (1925) 380.

The Three Classes of Emulsions.—Emulsions of silver halides in gelatin are conveniently divided into three classes:

1. *Emulsions with an excess of silver nitrate.* In this class are found all emulsions designed for printing-out. A typical example is gelatino-chloride printing-out-paper. With the virtual abandonment of printing-out-papers, this class of emulsions is of little importance.
2. *Emulsions with a considerable excess of soluble halide.* The best example of an emulsion of this character is the unwashed silver chloride emulsions employed for slow developing papers such as Velox, etc.
3. *Emulsions with a slight excess of soluble halide.* In this class belong all ordinary negative emulsions.

Emulsification.—The precipitation of the silver halide is a very important and exacting operation. The crystals of silver halide must be of the proper size and must not flocculate together and separate out but remain uniformly dispersed in the gelatin solution. The characteristics of the emulsion are very largely determined by the conditions existing during emulsification. This is particularly true of emulsions of low sensitivity and those designed for papers, in which the after processes of ripening or digestion are of little importance. In the case of negative emulsions, processes subsequent to emulsification may

[6] See Sheppard, *Gelatin.*

Baker—Making Bromide and Chloride Papers. Amer. Phot. **34** (1940) 469, 472.

Charriou and Valette—Researches on Silver Chloride Emulsions. Proc. Ninth Int. Congress of Phot. Paris. 1935.

Charriou and Valette—Positive Photographic Emulsions. Phot. J. **76** (1936) 407–410.

Leroy—Preparation of Fine-Grain Plates. Brit. J. Phot. **77** (1930) 125.

Preparing Unwashed Silver Chloride Emulsions. Phot.Tech. **1** (1939) Nov. p. 41.

Prileshaeff—Preparation of a Bromide Paper Emulsion. Phot. Korr. **68** (1932) 150–152.

Renwick—Note on the Factors Affecting Grain Size in Photographic Emulsions. Phot. J. **64** (1924) 324.

Steigmann—A High-Contrast Ammonia-Type Emulsion Rich in Silver Bromide. Phot. Korr. **71** (1935) 165.

Steigmann—Extra-Contrasty Positive Ammoniacal Gelatinobromide Emulsion. Phot. Korr. **71** (1935) 156.

Steigmann—Green and Brown Developing Emulsions. Phot. Ind. **34** (1936) 764–766.

result in greatly increased sensitiveness, but it is not possible to convert a low speed emulsion of the positive type into one of high speed simply by digestion; an emulsion of high speed will be obtained only if the conditions of precipitation are favorable to the growth of silver halide grains of high sensitivity.

The conditions which affect the size of the crystals of silver halide formed upon precipitation and thus the photographic characteristics of the emulsion are (1) the concentration of the gelatin solution in which the precipitation of the silver halide occurs; (2) the concentration of alkaline halide during precipitation; (3) the rate of addition; (4) the temperature and (5) the presence of ammonia or ammoniacal silver oxide. Quantitative data are lacking on all of these factors. Such data as may be available are known only to emulsion-makers and only general statements are to be found in recent literature on the subject of emulsions.

Curves published by Sheppard[7] indicate a definite relationship between the concentration of the gelatin solution in which the silver halide is precipitated and the average size of the grain. It is well known that only a part of the gelatin is present during emulsification and that in the case of high-speed negative emulsions the concentration of the reactants is higher and that of the gelatin lower than in low-speed emulsions. The grain size is affected also by the physical properties of the gelatin but again quantitative data are lacking.[7a]

In emulsions designed for development, the amount of alkaline halide present during precipitation is invariably greater than is necessary to combine with the silver salt to form silver halide. The presence of excess soluble halide during precipitation is essential in the preparation of high speed negative emulsions. Silver bromide is more soluble in the solutions containing a soluble bromide and the increased solubility results in the formation of larger and more sensitive grains. An excess of soluble halide also has the effect of reducing the danger of fog in the preparation of highly sensitive emulsions.

The usual practice in emulsification is to add the silver salt to the alkaline halide in gelatin; however, in the preparation of emulsions employing silver chloride there is less danger of flocculation if the chloride solution is added to a gelatin-silver nitrate solution.[8] The reason for this is unknown.

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[7] *Brit. J. Phot.* **69** (1922) 679.

[7a] Sheppard and Trivelli found that there is a direct proportionality, under given conditions of precipitation, between the time factor and the average grain size. *Phot. J.* **79** (1939) 330.

In some of the formulas given in Wall's *Photographic Emulsions* the alkaline halide (potassium bromide) and silver nitrate are added to the gelatin at the same time, the former, of course, being in excess. Since in this case the concentration of bromide is more nearly constant than when the two are added separately, it would appear to tend towards a more uniform grain-size.

The favorable influence of ammonia on ripening was observed in 1879 [9] by Monckhoven who called attention to the fact that an emulsion might be ripened by the addition of ammonia instead of heat. Ammonia may be added to the emulsion as ammoniacal silver oxide in the process of emulsification or at a later stage. The presence of ammonia during emulsification results in a change in the crystal habit of the precipitated silver halide; the thin plate-like crystals not only become thicker and more rounded but tend [10] to clump together. Ammonia added to the emulsion after emulsification does not change the crystal habit of the grains already formed but does facilitate the ripening process. (See Ripening.)

Bromo-Iodide Emulsions.—The addition of iodide to gelatin-bromide emulsions was advised by Penney in 1878 and studied in detail by Abney and Eder. According to Abney [11] it is essential for high speed emulsions. The use of iodide makes possible a higher degree of ripening and thus indirectly leads to emulsions of higher sensitivity. According to Carrol [12] the sensitivity of such emulsions is not realized unless they are ripened further. Although silver iodide is less soluble than silver bromide and would for this reason be precipitated first under ordinary conditions, Sheppard and Trivelli found no grains

[8] Eder, *Handbuch* **III**, 5th Ed. 1903.

[9] *Phot. Korr.* **16** (1879) 197.

[10] Carrol, "The Preparation of Photographic Emulsions," *J. Chem. Ed.* **8** (No. 12, December, 1931) 2341.

[11] *Phot. News* (1880) 174, 196.

[12] Carroll, *J. Chem. Ed.* **8**, No. 12 (Dec., 1931) 2341.

TRIVELLI AND SMITH—Action of Silver Bromide on Silver Iodide Emulsions. Phot. J. **78** (1938) 644.

TRIVELLI AND SMITH—Effect of Grain Size on the Finishing of Photographic Emulsions. Phot. J. **79** (1939) 609.

TRIVELLI AND SMITH—The Effect of Silver Iodide upon the Structure of Silver Bromo-iodide Precipitation Series. Phot. J. **80** (1940) 285.

of silver iodide in a bromo-iodide emulsion.[13] Renwick and Sease found [14] that the larger grains contain more iodide. The x-ray diffraction studies by Wilsey show that the grains of a mixed bromo-iodide emulsion have the same type of lattice structure as those of silver bromide alone.[15] It appears, therefore, that the grains of the bromo-iodide emulsion may be looked upon as a mixture of silver bromide and iodide.

Huse and Muelendyke [16] found that the addition of iodide results in a shift in the spectral sensitivity of the emulsion towards the longer wave lengths and it is reasonably certain that silver-bromo-iodide emulsions absorb more energy from white light than those of silver bromide alone. This alone, however, does not account for the increased sensitivity. In the opinion of Trivelli [17] the increased sensitivity is due to the strain set up by the presence of the silver iodide incorporated in the crystal structure of the silver bromide.

Ripening.—After emulsification, all emulsions, except those for printing papers, are subjected to a process known technically as ripening, the purpose of which is to increase the sensitiveness to white light. Ripening is accomplished by keeping the emulsion at a relatively high temperature for a certain time, by the addition of ammonia, or both, although, when ammonia is added, the temperature must be lower if fog is to be avoided. Ripening results in a change in the number and size of the grains of silver halide present in the emulsion and in their composition. In the presence of a solvent such as free bromide, an increase in temperature causes the smaller grains to disappear and combine with the larger ones; although the number of grains present is thus reduced the average grain size is increased.[18] It was long

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[13] Sheppard and Trivelli, *The Silver Bromide Grain of Photographic Emulsions.* D. Van Nostrand (1921).

[14] *Phot. J.* **64** (1924) 360.

[15] Wilsey, *J. Frank. Inst.* **200** (1925) 739.

[16] *Phot. J.* **66** (1926) 306.

[17] *Rec. tran. Chem.* (4) **5** (1924) 360.

[18] Sheppard and Lambert, *Colloid Symposium Monograph,* **4** (1926) 281; **6** (1928) 265, Chemical Catalog Co., New York.

Baldsiefen, Sease and Renwick—Silver Iodide in Photographic Emulsions. Phot. J. **66** (1926) 163–184.

Price—Silver Iodide and Sensitivity. Phot. J. **75** (1935) 447.

Steigmann—The Silver Iodide Problem. Phot. Ind. (1929) 375–376.

Trivelli—Influence of Silver Iodide on the Sensitivity of Silver Bromide. J. Soc. Chem. Ind. **42** (1932) 908.

supposed that the increase in sensitiveness produced in the ripening process was the result of the increased grain size, for it is well established that in general the large grains are more sensitive than the small.[18a] Sensitivity is not a function of grain size alone, however, and the increased size of the grains in the emulsion is a necessary but not a sufficient condition for high sensitivity.

Coincident with the change in the size of the crystals of silver halide is a change in chemical constitution. One result of the ripening process is probably the reduction of a part of the silver halide to colloid silver.[19] The recent work of Sheppard on the sensitivity promoting substances in gelatin, while it does not exclude the possibility of the formation of colloid silver as one of the factors in ripening, indicates that an important, if not the primary, factor is the conversion of the allyl isothiocyanates, or other sensitizing substances present in gelatin, to thiocarbamide which, in turn, reacts with a portion of the silver bromide to form sensitivity centers, or nuclei, on the silver halide crystal. The way in which these centers of silver sulfide promote sensitivity is not entirely clear; the various theories which attempt to explain the mechanism involved will be discussed later.[20]

[18a] Trivelli and Smith found that speed as measured by the H and D method increases to a greater degree in the digestion of small-grain emulsions than those of larger average grain size. *Phot. J.* **79** (1939) 609.

[19] Renwick, *J. Soc. Chem. Ind.* **156T** (1920) 39; *Brit. J. Phot.* **67** (1920) 447, 463.

[20] See Sheppard and Trivelli, *The Silver Halide Grain of Photographic Emulsions* (Monographs on the Theory of Photography). D. Van Nostrand Co., New York.

Carroll and Hubbard—Photographic Emulsion: Silver-Ion and Hydrogen-Ion Concentrations and Sensitivity. Bur. Stand. J. Res. **8** (1932) 481.

Lialikov, Piscounova, Chipilov, and Tcherdyncev—Digestion of Photographic Emulsions. Proc. Ninth Int. Congress of Phot. Paris, 1935.

Rawling and Glassett—The Sensitivity of Photographic Emulsions. I. The Effect of Changing Hydrion Concentration during the Washing and Digestion Stages. Phot. J. **66** (1926) 495–504.

Rawling—II. Hydrion Concentration and the Silver Bromide-Thiocarbamide Complexes. Phot J. **67** (1927) 42–48.

Tschibissof—Digestion of Photographic Emulsions. Proc. Ninth Int. Congress of Phot. Paris, 1935.

Wada—Ripening of Photographic Emulsions. Variation of the Characteristics of the Emulsion during the First Ripening. J. Soc. Chem. Ind., Japan **42** (1939) 42.

The function of ammonia in ripening is apparently closely connected with the formation of the sensitizing substances such as allylthiocarbamide described by Sheppard and Punnett.

Under given conditions of digestion the sensitiveness varies with the hydrogen-ion concentration. With a given emulsion the sensitiveness increases with increasing time of digestion to a maximum point which varies with the pH (or hydrogen-ion concentration).[21]

While it might be concluded that the change in sensitiveness with hydrogen-ion concentration is due to the amount of silver sulfide derived from the silver bromide-thiocarbamide reaction, this does not seem to be entirely the case, for it has been demonstrated that the sensitiveness of an emulsion, which is lowered upon the addition of acid, is immediately restored when the hydrogen-ion concentration is brought back to its original value.[22]

Eliminating the Soluble Salts.—After ripening, the emulsion is chilled and the gelatin sets to rather stiff gel. It is then shredded and washed in cold water to remove the alkaline nitrate formed in the precipitation of the silver halide and the excess halide and ammonia (when the last mentioned is used). The excess salts may be left in dilute silver chloride emulsions as used for contact printing papers, but other emulsions must be washed to prevent the salts from crystallizing out and also because they act as desensitizers.

The emulsion is placed in a press the bottom of which consists of a netting of silver wires. The pressure forces the jelly through the interstices of the wires breaking it up into fine shreds or "noodles" which are washed in cold running water. The quality of the water is a very important factor. It must be free of metallic or organic substances which would produce undesirable reactions. The alkalinity is also important. A moderately hard water is desirable as it tends to prevent the swelling of the gelatin. For this reason the temperature of the wash water must be kept relatively low, not above 10° C.[22a]

The ammonia and alkaline nitrate must be eliminated as completely as possible or the emulsion will possess poor keeping qualities. The soluble halide, on the other hand, must not be eliminated completely for experience has shown that the presence of a small amount has a favorable influence on the keeping qualities of the emulsion. Emulsions free of soluble halide develop fog in a relatively short time. The effect is more pronounced in the case of highly sensitive negative materials which by their very nature must be relatively unstable.

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[21] Rawling and Glassett, *Phot. J.* **66** (1926) 495.

[22] Rawling, *Phot. J.* **67** (1927) 42. Sheppard and Wightman, *Phot. J.* **69** (1929) 22.

[22a] F. J. Shepherd and Ilford Ltd. patented the freezing of the emulsion to facilitate washing. B.P. 313,631 of 1927.

After-Ripening or Digestion.—At this stage, it is usual to add the remainder of the gelatin required for the completed emulsion, after which the emulsion may be again heated, usually at a lower temperature than before; a process known as after-ripening or digestion. This second heat treatment, unlike the first, has but little effect on the size of the silver grains but increases the sensitiveness and contrast of the emulsion. The increase in sensitiveness is very marked in the case of neutral emulsions and those containing iodide.[23]

The increased sensitiveness is apparently connected with the formation of the sensitivity centers, or nuclei, of silver sulfide. The formation of silver sulfide from thiocarbamide, and possibly from other sensitizing substances, is retarded by an excess of bromide. This tends to lend support to the theory that the reaction taking place during after-ripening or digestion is primarily one between the sensitizing substances and the silver halide producing sensitivity centers, or nuclei, of silver sulfide.

The rate of digestion increases with the hydrogen-ion concentration, and for a given emulsion the sensitiveness varies with the time of digestion to a maximum which varies with the pH.[24]

Digestion must be carried out with great care in the case of high-speed negative emulsion in order to obtain high sensitiveness and the necessary contrast without fog.

Additions Prior to Coating.—If the emulsion is to be kept in storage for some time before coating, a preservative such as thymol, salicylic acid, or phenol is added to prevent bacterial growth which would cause decomposition of the gelatin. It is then chilled and placed in storage where it is kept at a relatively low temperature.

It has become a part of the commercial practice in the preparation of emulsions to add at various stages, but apparently chiefly immediately

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[23] Carroll and Hubbard, *Bur. Stand. J. Research* **7** (1931) 219.

[24] Rawling and Glassett, *Phot. J.* **66** (1926) 495; Rawling, *Phot. J.* **67** (1927) 42; Sheppard and Wightman, *Phot. J.* **69** (1929) 22.

CARROLL AND HUBBARD—The Photographic Emulsion: After-Ripening. Bur. Stand. J. Res. **7** (1931) 219–259.

RAWLING—Effect of Thiocarbamide during After-Digestion. Proc. Ninth Int. Congress of Phot. Paris. 1935.

prior to coating, certain substances, known in the trade as "doctors," to harden the emulsion, to promote flexibility, to prevent or reduce fog and to improve the keeping properties, or to increase sensitivity.[25] Many of the substances are undoubtedly trade secrets; the patents granted in recent years, however, provide some information on the general direction of developments in this field.

The addition of chrome alum, formaldehyde and acrolein, all in small quantities, for the purpose of hardening the gelatin layer and preventing its softening and frilling in hot weather, has long been common practice. The use of these gelatin hardening agents, however, tends frequently to cause brittleness and a lack of flexibility, which apparently has been overcome, in part at least, by the addition of glycerol. In recent years patents covering the use of a comparatively large number as emulsion hardeners have been granted among which may be mentioned diacetyl, acetyl benzoyl, acetyl caproyl (B.P. 444,289, Kodak Ltd.), aldehydes (B.P. 504,378, Kodak Ltd.); hydroxyaldehydes and di-aldehydes, as well as the aldehyde-ketones (B.P. 463,427, Kodak Ltd.); glyoxylic and formylacrylic acid (B.P. 499,648, I. G. Farbenindustrie); dioxyacetone, fructose and p-oxybenzoyl (B.P. 497,023, I. G. Farbenindustrie); mucobromic and mucochromic acid (U.S.P. 2,080,019, Eastman Kodak); 2-selenomercapto-4-hydroxypyrimidine and alkyl, aralkyl, aryl and arylene derivatives (U.S.P. 2,195,150 Kendall).

A large number of patents have been granted for substances which are described as "fog preventatives" or "stabilizers." Presumably substances of the first class tend to restrain fog in the emulsion while those of the second class act as stabilizers in the sense that they prevent the growth of fog in storage or after coating.

The use of 6-nitro-benziminazole and several similar substances both as additions to the emulsion and in developers has been described by Trivelli and Jensen (*J. Franklin Inst.* **210** (1930) 287); phenyl morpholine (U.S.P. 2,143,802 and 2,150,702, Sheppard, Vanselow and Eastman Kodak Co.); 2-mercapto-4-hydroxypyrimidine and selenomercapto-hydroxypyrimidine (U.S.P. 2,232,707 and B.P. 516,005 Kendall); ethylene diamine hydrochloride (U.S.P. 2,113,312, Vittum and Eastman Kodak Co.); thiothiazolidine (F.P. 788,511 Gevaert); phenylene diamines and benzidines (F.P. 821,618 Kodak-Pathé); selenic acid (B.P. 441,625, I. G. Farbenindustrie); guanine and anthrapyrimidines

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[25] Trivelli and Jensen, *J. Franklin Inst.* **210** (1935) 287; Middleton, *Brit. J. Phot.* **75** (1928) 512.

(B.P. 442,731, I. G. Farbenindustrie); di- and tri-amylamines (G.P. 600,843, I. G. Farbenindustrie); di-isoamylamine propyl-hexamylamine (B.P. 419,579, I. G. Farbenindustrie); di-o-formylethylamino-diphenyl-disulfide (U.S.P. 1,962,133, Brooker, Staud & Eastman Kodak Co.); diphenylamine and methyl-diphenylamine (U.S.P. 2,011,669, Zehlke & Agfa-Ansco), and buffer substances containing a carboxylic acid group, a sulfonic, a phenolic group or an enolic keto group (B.P. 492,257, of Kodak Ltd.).

The dyes necessary for rendering negative materials orthochromatic or panchromatic are also added at this stage. See Chapter VIII.

The Silver Bromide Grain of Photographic Emulsions.—When examined under a high power microscope, the photographic emulsion is seen to consist of numerous semi-transparent and practically opaque grains of silver halide imbedded in gelatin. These grains of silver halide are definitely crystalline (Fig. 203) [26] and of various forms and sizes; the most constantly recurring forms being triangles and hexagons, some of which are irregular, while all have rounded corners, but occasionally a long rod-shaped crystal is observed. The grains also vary in transparency, some being almost completely transparent while others are nearly opaque. Since the opaque grains behave in exactly the same way as the transparent grains, there is no justification for assuming that they are different substances. In addition to these there are ultra-microscopic grains which are beyond the limit of visibility with the highest power of the microscope. Recent investigation has shown that these are also crystalline and have substantially the same structure as those of larger dimensions. There is no evidence for the existence of non-crystalline silver bromide in photographic emulsions.

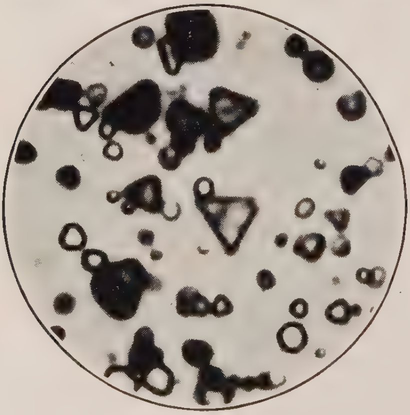

Fig. 203. Crystals of Silver Halide in a High Speed Photographic Emulsion.

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[26] The emulsion shown in Fig. 203 has been greatly diluted in order that the individual crystals may be more clearly seen. Ordinary emulsions as used for coating of plates and film consist of many layers of such grains and contain from 10 to 25 billion of such crystals to the square inch.

The size of the silver halide grains in commercial emulsions ranges from the ultra-microscopic particles of less than one micron to grains as large as 3 or 4 microns. In positive emulsions the larger number of grains are either ultra-microscopic or very small, while in the case of highly sensitive negative emulsions, although a large number of ultra-microscopic grains are present, the majority of the grains are of microscopic size, while all are of course definitely crystalline.

The Sensitivity of the Silver Halide Grain.—Microscopical investigation has shown that in spite of the enormous number of grains of silver halide and their close proximity to one another, each individual grain affected by light acts as a single unit and there is no transference of development from one grain to another, unless the two are grouped together in absolute contact; a state of affairs characteristic of some emulsions. It has also been found that a grain is either made developable by a certain amount of light or it is not developable. Thus, we do not get partial development for a certain exposure followed by more for a longer exposure but up to a certain amount of light action the grain is undevelopable and after that amount is reached it is rendered completely developable. The amount of light required to make a grain developable represents what is termed the *sensitivity* of the grain.

Investigation of the number of grains made developable by a given exposure shows that all the grains are not equally sensitive; because under such conditions all the grains would become developable as soon as the exposure reached a certain value. Microscopical examination at high powers shows that the grains of silver halide differ widely in size and on counting the number of grains made developable in given size-classes, it is found that in one and the same emulsion the sensitivity increases with the size of the grain. This does not necessarily mean that all large grains are more sensitive than smaller ones, for with different emulsions the reverse is often true, but if we keep to the same emulsion the larger grains are on the average more sensitive than the smaller. There are, however, differences in sensitivity among grains of the same size and shape in the same emulsion. Sensitivity is, therefore, not wholly a function of the size of grain, but is due to an inherent difference in the grain itself.

Long ago Abegg and Eder suggested that in the process of digestion a trace of the silver halide is reduced to either a sub-halide, or to silver. These traces they referred to as "ripening centers." These served as centers for further reduction by light to form the latent image. The existence of specially sensitive spots in the grain of silver halide is now well established. Lüppo-Cramer and Renwick supposed these spots, centers, nuclei, or specks, as they are variously termed, to consist of colloid silver. However, the work of Sheppard and his co-workers on the sensitizing substances in gelatin seems to prove beyond all doubt that the sensitivity centers are composed of silver sulfide, which is produced as a result of a chain of reactions between the sensitizing substance and the silver halide.

These submicroscopic specks of silver sulfide are distributed at random in, or on the surface, of the grains. It is believed that they cause a strain in the crystal of silver halide creating around them a sphere of weakness in the crystal structure which increases the sensitivity of the grains.

We will leave to a later chapter a discussion of the manner in which these sensitivity centers function in the formation of the latent image.

Grain-Size Distribution and its Relation to the Photographic Properties of Emulsions.—Investigation having shown that the individual halide grain is the photochemical unit of the photographic plate, the properties of the emulsion representing simply the sum of the properties of the individual grains modified by their positions in layers, a study of the effect of grain-size distribution in emulsions and its relation to photographic properties is of great importance. For if emulsion sensitiveness is merely a matter of grain-size distribution the emulsion maker has only to provide the conditions favorable to the growth of crystals of the proper size in order to produce emulsions of the highest possible sensitiveness or having any other required properties. On the other hand, should it be shown that photographic properties are not wholly, or only partially, controlled by grain-size distribution but by other factors as well, the line of investigation must naturally be directed along entirely different lines.

Before 1895 Haddon and Banks called attention to the probability of some relation between the size of grains and the sensitiveness of an emulsion and Mees in 1915 suggested that "inasmuch as emulsions are not homogeneous, but contain grains of all sizes, the sensitiveness of the emulsion will depend upon the distribution of the different sizes of grains, as will also the shape of the characteristic curve." [27] Slade and Higson as the result of some investigations on the action of light on an emulsion containing grains of very nearly the same size and only one layer thick also concluded that the properties of the emulsion are determined mainly by the relation of the different sizes of grains to one another and the quantity of each present.[28] Svedberg found that for every class of grains of nearly the same size in the emulsion there is a distinct characteristic curve.[29]

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[27] *J. Franklin Inst.* 179 (1915) 141.

The matter was not fully investigated until Sheppard, Wightman and Trivelli attacked the problem by photomicrographing the grains of various emulsions at a magnification of 2000 times and then enlarging the negative five times, so that the actual magnification equalled 10,000 times. The developed grains of a given area were then measured and divided into classes according to size. The data secured in this manner may be represented graphically by plotting the number of grains of each class as ordinates against the sizes of the grains as abscissae. In Fig. 204 are shown photomicrographs of the emulsion of a portrait film and a Standard slow lantern plate together with curves showing the size-

[28] *Phot. J.* **59** (1919) 260.

[29] *Z. wiss. Phot.* **20** (1920) 36.

Sheppard—Dispersity of the Silver Halides in Relation to their Photographic Properties. First Colloid Symposium Monograph, 1923.

Sheppard—Grain-Size and Distribution in Emulsions. Phot. J. **65** (1925) 31.

Sheppard, Wightman and Trivelli—Size-Frequency Distribution of Particles of Silver Halide in Photographic Emulsions and its Relation to Sensitometric Characteristics. I. J. Phys. Chem. **25** (1921) 181; II. Ibid. **25** (1921) 561; III. Ibid. **27** (1923) 1; IV. Ibid. **27** (1923) 141; V. Ibid. **27** (1923) 446.

Sheppard, Trivelli and Wightman—Relationship of Photographic Emulsion Fog to Grain Size. Phot. J. **65** (1925) 134.

Sheppard and Trivelli—Sensitivity of Silver-Halide Grains in Relation to Size. Phot. J. **67** (1927) 284–287.

Sheppard and Graham—Extragranular Factors in Photographic Sensitivity. Phot. J. **80** (1940) 472.

Silberstein and Trivelli—Relations Between the Sensitometric and the Size-Frequency Characteristics of Photographic Emulsions. J. Opt. Soc. Amer. **28** (1938) 441.

Svedberg—Size and Sensitiveness of the Grains in a Photographic Emulsion. Zeit. wiss. Phot. **20** (1920) 36.

Svedberg—On the Relation between Sensitiveness and Size of Grain in Photographic Emulsions. Phot. J. **62** (1922) 186.

Trivelli and Smith—Empirical Relations Between Average Grain Size of Photographic Emulsions and the Hurter & Driffield Speed. Phot. J. **79** (1939) 463.

Trivelli and Smith—Further Investigations in the Empirical Relations Between Speed and Average Grain Size of a Precipitation Series. Phot. J. **80** (1940) 381.

frequency distribution of each. It will be observed that the grains of the positive emulsion are all comparatively small and uniform, the range being from about 0.2 to 1 micron. The high speed portrait film, on the contrary, shows an extended range of sizes from about 0.2 micron to as high as 2.7 microns with a maximum close to 0.5.

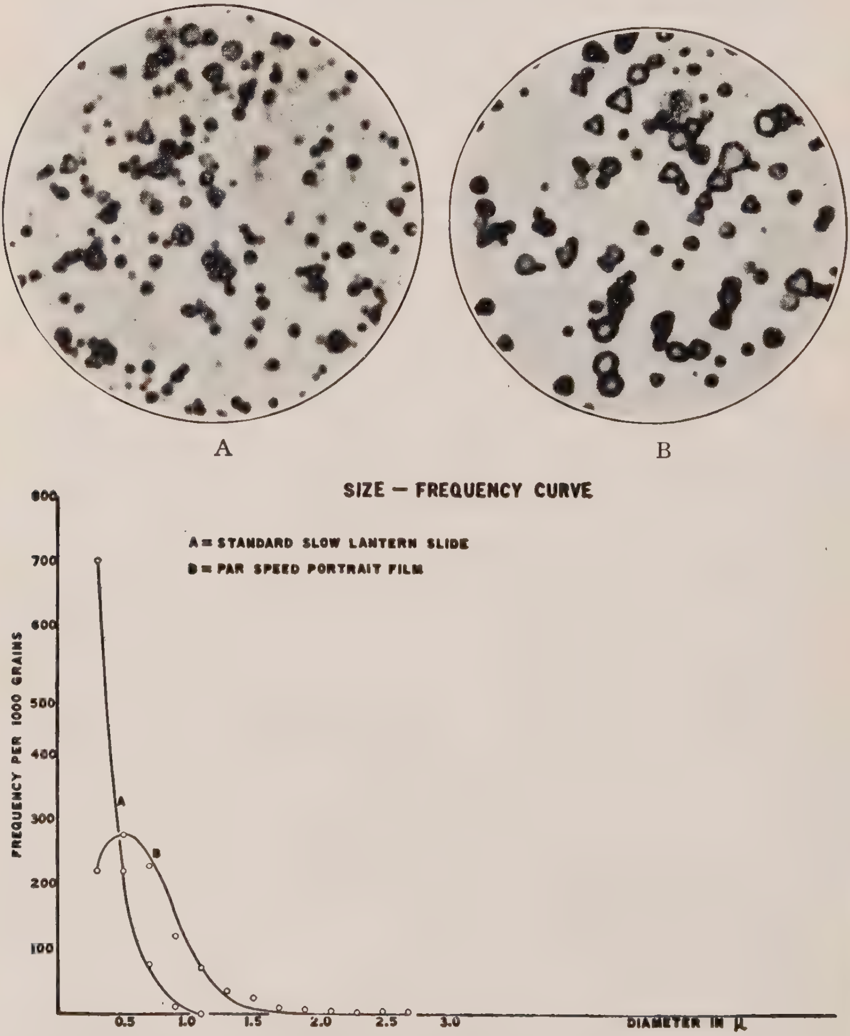

Fig. 204. Photomicrographs of the Emulsion of a Portrait Film and a Lantern Plate with the Size-Frequency Curve of Each.

Hypersensitizing of Emulsions.—The amount of exposure necessary to produce a developable image with a given film may be reduced by a number of methods. Such processes are known as hypersensitizing and involve the use of ammonia, ammoniacal silver chloride, mercury, and exposure to a weak source of light for a period of 30 minutes to one hour after exposure in the camera. In general, all methods of increasing speed, i.e., decreasing the necessary exposure by such means are less effective with high speed materials than with those of lower speed.

The following ammoniacal silver formula has been recommended[30] for increasing the speed of panchromatic materials for aerial photography:

Ammoniacal silver chloride	4 cc.
Distilled water	200 cc.

The ammoniacal silver chloride solution is made by dissolving 1.5 grams of silver nitrate in 50 cc. (23 grains in 2 oz.) of distilled water. Hydrochloric acid is then added as long as a white precipitate of silver chloride is formed. The clear solution is then poured off, the precipitate washed twice and then dissolved in 200 cc. of ammonia 0.190 (7 oz. 20 min.). The sensitizing solution, as prepared ready for use, will serve for six 9 × 12 cm. (3½ × 4¾ inches) plates or their equivalent. The films or plates should be immersed in the solution for 2 minutes at 65° F. (18° C.) and dried as rapidly as possible but without the use of heat. The time of exposure is reduced from 2 to 7 times, depending on the emulsion; but films so treated will keep only a day or two before they begin to show fog.

Dersch and Duir found that the exposure necessary with a negative material was reduced from 50 to 150% by exposing it to mercury for 20 to 30 hours at room temperature after exposure in the camera. Smethurst found that the increase in effective speed varies with the emulsion and English reported that the results vary widely with the emulsion and the humidity; no increase in effective speed being observable with a number of emulsions.[31]

If an emulsion after exposure is bathed in a dilute solution of hydrogen peroxide for a few minutes at room temperature an increase in effective speed is obtained. The increase in speed varies with the emulsion and in general increase with the pH. Thus far it has not been found practical as a means of hypersensitizing.[32]

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[30] Jacobsohn, *Amer. Phot.* 1929, 20; *Brit. J. Phot.* **76** (1929) 315.

[31] Dersch and Dürr, *J. Soc. Mot. Pict. Eng.* (1937). Smethurst, *Brit. J. Phot.* **84** (1937) 337. English, *Amer. Phot.* (1939) 90. Emmermann, *Brit. J. Phot. Almanac* (1938) 198. Hopkinson, *Brit. J. Phot.* **85** (1938) 183.

Quite recently it has been reported that the speed of a panchromatic material is increased from 2 to 4 times by a uniform exposure of from 30 to 60 minutes to light of such intensity as will produce a fog density of approximately 0.2, *after exposure in the camera.* The increase in effective speed is greater for low speed emulsions than for those of high speed and the contrast of the image is reduced slightly necessitating longer development. The increase in speed is not obtained with shorter times of exposure at higher intensity levels nor if the exposure is made *before* exposure in the camera.

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[32] Wightman and Quirk, *J. Franklin Inst.* **204** (1927) 731.

Moore—Hypersensitisation of the Latent Image at High Intensity by Uniform Low-Intensity Light Exposure. Phot. J. **81** (1941) 27.

CHAPTER VIII

COLOR SENSITIZING DYES FOR PHOTOGRAPHIC EMULSIONS

Leading authorities in the field of photography generally agree that the expansion of the methods of optical sensitizing has been one of the most important factors in the advancement of the technique of photographic emulsions. The chemical compounds which effect this sensitization process are found only in the class of substances known as dyes. The photographic sensitizers used before 1903 were chosen from synthetic dyes which were used for dyeing fabrics and other textile materials. After this time academic and industrial laboratories in Germany started research to obtain dyes having better photographic sensitizing properties.

Almost all of the research and production of sensitizing dyes and their intermediates up to 1914 was carried out under the control of two dye firms in Germany. The war of 1914–1918 developed a need outside of Germany for better sensitizers. This resulted in the creation of a program of research and production of sensitizing dyes in England which has been extended to the United States and other countries.

Most of the work on the development of the actual sensitizers, has been carried out in the laboratories of the photographic film manufacturing companies. Therefore, for obvious reasons the formulas used and much of the information is not available for general use. The patent literature is of course available but many of the patents granted both in this country and Europe are very brief and frequently contradictory. Thus, only those who have access to actual results of research in this field are qualified to write a complete treatise on sensitizing dyes. This chapter is a brief review of the literature.

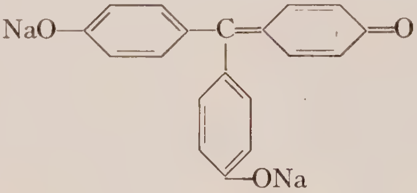
Classes of Sensitizing Dyes.—Sensitizing dyes, like other dyes, are divided into acid and basic classes.

The Acid Dyes.—The acid class includes certain dyes from the acid triphenylmethane dyes, such as corallin and erythrosin, the tetraiodothiaxanthenone and thianaphthenone

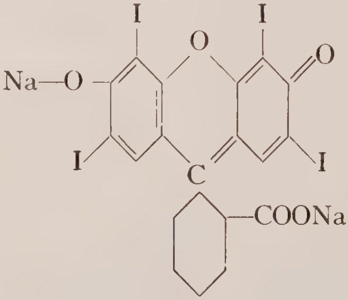
The Basic Dyes.—This class includes the cyanines, the merocyanines, the pinaflavols, the hemioxonols, the basic tri-phenylamines, and a group of dyes recently discovered which are closely related to the cyanines. There are a few more new types of compounds found in the very recent patent literature for which the patentees' claim sensitizing properties. However, it is obvious that they cannot be included in this somewhat brief treatment of sensitizing dyes.

Classification and Constitution of the Acid Sensitizing Dyes

The Triphenylmethanes.—This class includes Corallin (sodium Aurin), Eosin, Erythrosin and Rose Bengal. Corallin is of interest only because it was the dye Vogel used in 1873 to prevent halation in silver halide—collodion emulsions, and by so doing accidentally discovered the principle of sensitization. Its general formula is $(NaOC_6H_4)_2{=}C_6H_4{=}0$, and is produced generally by heating a mixture of phenol (carbolic acid) with oxalic acid and H_2SO_4. Its structural formula is:

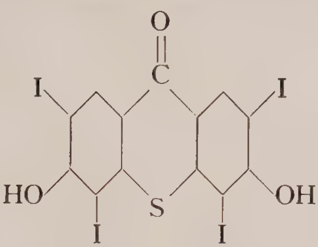


Erythrosin is of interest since it was used quite generally up to a few years ago either alone or in combination with other dyes as a sensitizer for the green. At the present time it has been largely replaced by the unsymmetrical and simple symmetrical cyanines of the selena, oxa and thia types and quite likely by the simple merocyanines. Erythrosin, like corallin, contains the hydroxyl or equivalent (—ONa) group, which characterizes them as of the acid type; in addition it contains a carboxyl (COOH) group. It is prepared by condensing 2 mols of resorcinol and 1 mol of phthallic anhydride to give fluorescein which is then converted to erythrosin by treatment with iodine. The structural formula of erythrosin is:



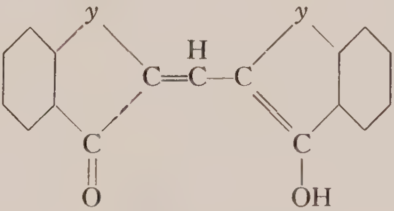
erythrosin

The Thiaxanthones.—These are keto type compounds and may be prepared by condensing 1 mol of formaldehyde with 2 mols of meta-aminothiophenol. The xanthones, or oxygen compounds, do not seem to be sensitizers. It is claimed in recent patent literature that the tetraiodo derivatives of the thia, selena and tellura-xanthones are good sensitizers for the spectral range of 520 to 610 $m\mu$ with a maximum of 565 to 580 $m\mu$. The structural formula of a typical compound is:



tetraiodothioxanthone

The Naphthenones.—These compounds are somewhat similar to the cyanines in general structure but do not contain nitrogen. They are prepared from compounds similar to indoxylic acid. It is claimed that their sensitizing maximum is 590 to 600 $m\mu$ and are therefore sensitizers for the orange. The following general formula will represent the class:



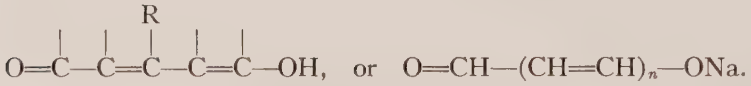
y = sulfur, selenium or tellurium

If y is sulfur; the dye is 3 (2) Thianaphthenone.[1] The oxythianaphthene and the oxyseleanaphthene rings respectively are condensed to form sensitizing dyes with the methine linkage by means of orthoformic acid ester in much the same manner as the quaternary salts of a heterocyclic base. Two heterocyclic groups linked by a methine, or series of conjugated methines, constitute the cyanines; a single heterocyclic base linked to a rhodanine type compound form the merocyanines. The naphthenone dyes form alkaline salts with good water solubility.

[1] G.P. 582,572; B.P. 416,664.

The sensitizing intensity is said to be relatively good for silver chloride, but only moderate for silver bromide. Thianaphthenone ring compounds from thioindoxylic acid are used as intermediates for the preparation of merocyanines.[2]

General Constitution of Acid Dyes.—As may be seen by examining the chemical structures of these compounds used as illustrations, a common feature in all of the classes given is a conjugated chain containing an odd number of carbon atoms, linking a ketonic oxygen and a hydroxy-oxygen, which may be represented diagrammatically as follows:



$$O{=}\overset{|}{C}{-}\overset{|}{C}{=}\overset{\overset{R}{|}}{C}{-}\overset{|}{C}{=}\overset{|}{C}{-}OH, \quad \text{or} \quad O{=}CH{-}(CH{=}CH)_n{-}ONa.$$

R may be H, an aryl (C_6H_5), or an alkyl (C_2H_5) group. The H of the OH group is usually replaced by sodium or potassium.

CLASSIFICATION AND CONSTITUTION OF THE BASIC SENSITIZING DYES

The Cyanines.—The cyanines proper, as a general class, are probably the most important sensitizing dyes. They comprise the largest number of satisfactory sensitizers used in present day emulsions. The cyanines are characterized by containing a quaternary nitrogen in a heterocylic nucleus, with or without a condensed ring (or rings) connected or linked by a conjugated chain, with an odd number of carbon atoms, to a ternary nitrogen in another nucleus of the same or or similar constitution as the nucleus containing the quaternary[3] nitrogen. The linking chain may be substituted or unsubstituted.

History of the Chemistry of Cyanines.—The first cyanine dye was prepared by Williams of England in 1856 or about the time Perkins prepared mauve, the first *aniline* dye. Williams, like Perkins, was interested in substances to be used for dyeing fabrics. The cyanine prepared was very impure, since it was prepared indirectly from a mixture of compounds obtained from coal tar of which quinoline no doubt was the chief ingredient. Nothing was known at that time of the chemical constitution of either quinoline or the blue dye known as "quinoline blue." The dye was unsatisfactory for dyeing fabrics since it was easily bleached by light, but about 20 years later

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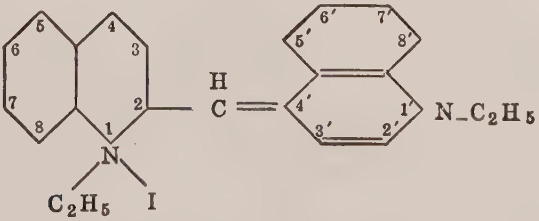
[2] U.S.P. 2,170,806.

[3] For a discussion of the terms "quaternary" and "ternary" the student is referred to *The Chemistry of Organic Compounds* by Conant.

Vogel discovered that it sensitized silver halide-collodion emulsions. It proved generally unsatisfactory as a sensitizer, although the original preparation did extend the spectral range to the orange.

The first important development in the chemistry of cyanines was the determination of the structure of quinoline and its subsequent synthetic preparation by Skraup in Germany about 1875. In 1883 German and Dutch investigators (Spalteholtz, Hoogewerff and Van Dorp) showed independently that Williams' cyanine and its analogues are condensation products formed by the action of caustic alkali and air oxidation on an equimolecular mixture of the alkyl iodides of quinoline and lepidine (see intermediates); although they did not know the true structure of this type of dye at that time. About 1883 these same German and Dutch investigators independently discovered the isocyanines. They were prepared by the action of caustic alkali and air oxidation on a mixture of the alkyl halides of quinaldine (see intermediates) and quinoline respectively. However, the actual chemical constitution, or structure of the isocyanines remained largely unknown until the classic work of Mills and Wishart of England about 1920. These dyes attracted little attention until about 1903 when Miethe and Traub took out a patent[4] on the application of the simplest isocyanine (Ethyl Red) as a sensitizer. The name used in the patent was Ethyl Red which 20 years later was shown to be 1, 1′-diethyl 4′-quinoline-2-quinaldine iodide or 1, 1′-diethylisocyanine iodide; the iodine atom is retained on the quinaldine part of the finished dye. The structure of ethyl red is:



About 1903 E. König of the Hoechst (M.L.B.) Dye Works started to modify ethyl red with the aim of obtaining better sensitizers, hence he and his associates were probably the earliest chemical investigators of the photographic sensitizers. Various isocyanines were soon put on the market[5] under the names Orthochrome T, 1:1′-diethyl 6:6′-

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[4] D.R.P. 142,926 of 1903.

[5] G.P. 167,159, 167,770.

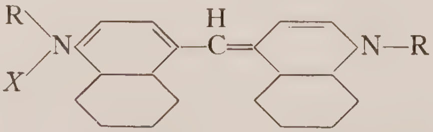
dimethyl isocyanine iodide; Pinaverdol (M.L.B.) or Sensitol Green (Ilford), 1 : 1′ : 6-trimethylisocyanine; Pinachrome, 1 : 1′-diethyl-6-ethoxyisocyanine.

In 1903 Bayer at Elberfeld proposed the dialkyl sulfates and the alkyl para toluene sulfonates in place of the alkyl iodides in order to increase the solubility of these dyes in water. They introduced the isocyanines as Homokol, Isokol and Perikol. The method employed in the production of these dyes was fundamentally the same as used by König and is illustrated in the preparation of Homokol: tolylquinaldine was treated with dimethyl sulfate to give a compound similar to quinaldine alkyl halides, which is then condensed with quinoline ethyl toluene sulfonate in alcoholic KOH solution to give the actual dye.

In 1905 E. König discovered that if formaldehyde is added to the reaction mixture used for the preparation of isocyanines, a blue dye is formed. The substance so produced was named *carbocyanine* about 15 years later by Pope and Mills of England. König had not recognized at the time that a new type of the cyanines had been produced as he had assumed the dye prepared was another isocyanine.

At the outbreak of the 1914–18 War the study of sensitizing dyes for panchromatic plates and aerial photography was undertaken by Pope and Mills [6] at Cambridge, England. The demand for these dyes by the allied air forces was not only met by this work, but the further investigations of this school led to improvements in the preparation of known dyes and particularly so to the development of the constitution and structure of many of the cyanines dyes.

Simple Cyanines.—In 1912 Kaufmann and Vonderwahl [7] of Germany suggested the formulas now accepted for the simple cyanines which are derivatives of quinoline, but Mills and Pope and their co-workers actually proved the structure of the cyanines and isocyanines by analysis of the decomposition products. Mills and Pope [8] showed that the general structure of "cyanine" or lepidine-cyanine which is the 4 : 4′-cyanine compound is represented by:



lepidine-cyanine or "cyanine"

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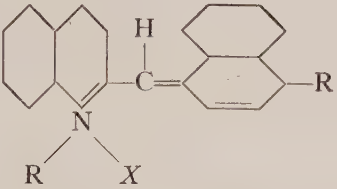
[6] *Phot. J.* **44** (1920) 183,253.

[7] *Ber.* **45** (1912) 1417.

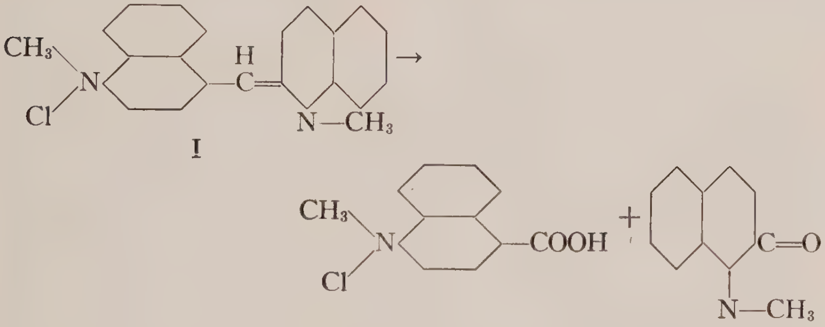
[8] *Phot. J.* **60** (1920) 183–202.

where R is alkyl and X = halogen. These lepidine-cyanines or "cyanines," as originally known, have very little importance today.

Mills and Wishart[9] proved that the isocyanines which are the 2:4′ and 4:2′ compounds have the general formula:



They proved it by oxidizing 1:1′-dimethyl isocyanine (I) to form 1-methyl-2-quinoline (11) and the methyl chloride of cinchoninic acid (III):



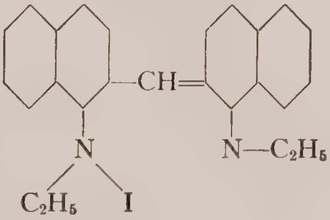
I

III

II

The isocyanines have been replaced to some extent by other types of dyes.

The formation of the 2,2′ carbocyanines from the quinoline ring was probably first observed by Kaufmann and Vanderwahl in 1912. However, Fischer and Scheibe[10] showed that this dye as prepared was the simplest 2,2′ carbocyanine and suggested the following as its structure:



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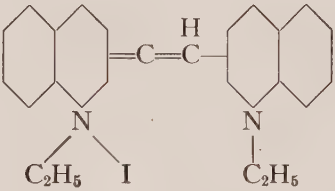
[9] *J. C. S.* **117** (1920) 579.

[10] *J. Prakt. Chem.* **100** (1920) s. 86.

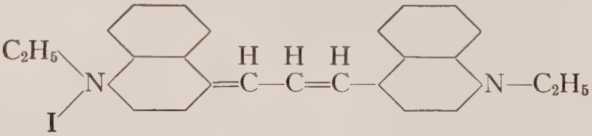
Fischer proposed calling this class the pseudo-isocyanines, which was later simplified to " pseudo-cyanines " and still later to ψ-cyanines.

Pinacyanol.—Mills and Hamer[11] showed that *pinacyanol,* which was first prepared by E. König in 1905, contains two quinoline nuclei joined by a chain of 3 methine (=CH—) groups at the 2:2′ positions. Wise, Adams, Stewart and Lund of the United States[12] had suggested that it contained two quinoline nuclei joined by a single methine group at the 4:4′ positions. Fisher of Germany[13] suggested the following:



Mills and Hamer, however, proved these formulas incorrect by showing that: (1) Fischer's formula was not in accordance with the analytical results and the " American " formula represented it as a true cyanine (lepidin-cyanine) which was not in accordance with its sensitizing action. W. König, in an article on the pinacyanols,[14] confirmed the structure assigned by Mills and Hamer.

Kryptocyanine.—The 4:4′ carbocyanine structure from two quinoline nuclei was first prepared in 1919 by Adams and Haller[15] of the U.S.A. Bureau of Chemistry who named it *Kryptocyanine.* It was formed by condensing two lepidine quaternary salts with formaldehyde. Mills and Braunholtz[16] proved its structure to be:



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[11] *J. C. S.* **117** (1920) 1550.

[12] *J. Ind. & Eng. Chem.* **11** (1929) 460.

[13] *J. prakt. Chem.* (II) **98** (1918) 204.

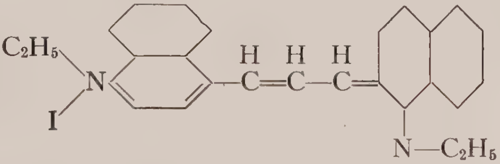
[14] *Ber.* **15** (1922) 3293–3313.

[15] *J. A. C. S.* **42** (1920) 266.

[16] *J. C. S.* **123** (1923) 2804.

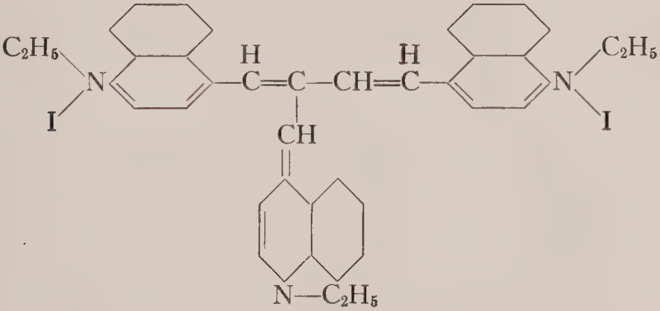
The introduction of kryptocyanine opened up the field of extreme red and near infra-red sensitivity in that it sensitizes very strongly although it has the disadvantage of not sensitizing beyond 800 mμ.

Dicyanine.—This dye was first prepared and introduced in 1906 by the Hoechst Dye Works. It was used as a sensitizer for the infra-red for many years before its structure was determined by Mills and Adams[17] in 1924. Its constitution is known to correspond to that of a 2:4′-carbocyanine, having the formula:



It sensitizes as far as 960 mμ. However, it is quite unstable and difficult to use.

Neocyanine.—This dye which is formed in the preparation of kryptocyanine was, up to the end of 1931, the best known sensitizer for the extreme infra-red, and with it the furthest extensions of the spectrum were photographed. It was first recognized in 1925 by H. T. Clarke of Eastman Kodak Co. Hamer[18] investigated its structure and has assigned the following formula to its ethiodide.



The Cyanines of Five Membered Rings.—The earliest representative of this class of dye was discovered by A. W. Hofmann in 1887.[19] Mills[20] of England rediscovered this dye in 1922 and found that under the influence of pyridine a dye is formed by the condensation of a benzthiazole and a 2-methyl-benzthiazole ring respectively. There was a mixture of dyes which contained chiefly a carbocyanine of the benzthiazole ring. Little progress was made in this field, however, until W. König [21] applied the ortho-formic acid ester synthesis, which simplified the condensation of the quaternary salts of 2-methyl-benzthiazole to carbocyanines. König's synthesis of ortho-formic acid ester was soon applied to the benzoxazole ring dyes [22] by Clark [23] in England, and by various workers to the dyes containing the methylized indol ring condensed with the benzene ring.

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[17] *J. C. S.* 125 (1924) 1913.
[18] *J. C. S.* (1928) 1472.
[19] *Ber.* 20 (1887) 2262.
[20] *J. C. S.* 121 (1922) 455.

Up to 1927 the reactive group, or atom, in the quinoline and condensed five membered ring compounds was the methyl group or halogen atom attached to the alpha (2) or gamma (4) carbon atom relative to the ring nitrogen in case of quinoline, and to the alpha carbon in the five membered rings. In 1927, R. Walter in Germany showed that mercapto or thio alkyl ether (—SR) possesses an extraordinary reactivity with active methyl groups. This method was applied to the preparation of all types of cyanines, especially 2,2′ and also 2,4′ monomethines (carbocyanines) with a great improvement in yield.

The selena ψ-cyanines [24] in particular have proved to be more energetic sensitizers than erythrosin and retain their sensitizing power even in the presence of stabilizing agents such as KBr. Thus it was possible to prepare commercially an orthochromatic emulsion of high general sensitivity. These selena and other cyanines have almost completely replaced erythrosin.

Other methods of condensation have been discovered within the last few years which have increased the yields of some and permitted preparation of other dyes which previously could not be prepared by older methods or if prepared could not be recovered from the reaction mixture. The various methods of preparation of the five membered ring compounds, with or without condensed rings, have been extended to dyes containing ring systems almost unknown ten years ago. New dyes, and improvements of old, are constantly being made until it seems that the field must be covered except for certain improvements in yields, nevertheless new dyes appear in the patent literature with frequent regularity.

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[21] D.R.P. 410,487 of 1922.

[22] König and Meier, *J. prakt. Chem.* **109** (1925) 324.

[23] L. M. Clark, *J. C. S.* (1928) 2313.

[24] Walter and Durr, D.R.P., 631,287, 658,192 of 1931.

Recent Progress in Infra-Red and Polymethines.—In 1912 W. König [25] prepared an acetal of certain aldehydes such as propargyl aldehyde and beta-ethyoxy acrolein, and also indicated a method for the preparation of carbocyanines with a carbon chain of more than three carbons. Evidently the methods employed by König were not successful since the first long carbon-chain dye did not appear in the literature until about 1930, when Beattie, Heilbron and Irving [26] discovered a group of dyes and named them dicarbocyanines; the linkage is through a five-carbon chain. Kendall [27] also prepared a dicarbocyanine about 1931 from quaternary salts of heterocyclic compounds by use of an acetal of propargyl aldehyde.

The next important development in infra-red sensitization was in the preparation of the tricarbocyanines almost simultaneously by three independent groups of workers of whom Wahl in Germany was the first,[28] Miss Hamer of England [29] and Piggott and Rodd also of England. The work of all three groups is based, first on the work of Zincke and his co-workers in Germany about 1904, who showed that a long chain carbon compound such as glutaconaldehyde could be prepared in a very unique manner, and second, on the "displacement process" of König (see preparation of polymethines).

Tetra and pentacarbocyines or those containing a chain of nine and eleven carbon atoms respectively have been prepared by methods similar to those used in the tricarbocyanines. These chains of the first tetra and pentacarbocyanines contained the oxyacyl group in the side chain. It was prepared by condensing two benzthiazole nuclei with a ketonic acid. The chain contains a ketonic oxygen. Recently tetra and pentacarbocyanines have been prepared with unsubstituted methine chains. The most recent development is that of O. Riester of Germany [30] who has produced a benzthazoline dye containing a chain of fifteen carbon atoms.

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[25] *J. prakt. Chem.* **85** (1912) 519; **86** (1912) 173.

[26] *J. C. S.* (1932) 260; B.P. 353,887 of 1930.

[27] B.P. 390,808.

[28] D.R.P. 499,967 of 1928.

[29] B.P. 351,555 and 354,826 of 1930.

[30] *D. Anm.* I 57303 IV a/22e; F.P. 834,718 of 1938.

Cyanines Classified

The Simple Cyanines.—They consist of two heterocyclic nuclei which are linked together by a single methine (=CH) group.

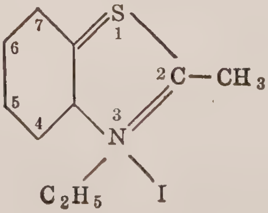
The quino and pyrido cyanines, which are derivatives of quinoline and pyridine respectively, are divided into the three classes: *cyanine, isocyanine* and *pseudo* or ψ-cyanines.

Cyanines.—They are characterized by the 4,4′ carbon linkage (see History of Cyanines) and may consist of two quinoline nuclei, of two pyridine nuclei, or of one quinoline nucleus and one pyridine nucleus respectively. Some of these combinations have not been made but are theoretically possible. They are important chiefly from an historical viewpoint.

Isocyanines.—These dyes contain the 2:4′ or 4:2′ linkage; like the cyanines they may consist theoretically of a variety of combinations using the quinoline and pyridine nuclei with or without condensed rings. So far as is known only the quinoline derivatives have been prepared. Ethyl Red, Pinaverdol and Pinachrome are in this class.

Pseudo or ψ-Cyanines.—These are the corresponding 2,2′-compounds and like the cyanines and isocyanines may include a variety of combinations using the quinoline nucleus and the pyridine nucleus with or without condensed rings. Like the cyanines and isocyanines the quinoline derivatives were the first to be prepared. Hamer and Kelly[31] of England have described dyes containing pyridine and beta-naphthoquinoline. The patent literature shows that other combinations have been made. These dyes are not as important as the various compounds containing one or two 5-membered heterocyclic rings.

Heterocyclic 5-membered Ring Symmetrical Thiazoles.—It is obvious from a consideration of the structure of thiazole with or without a condensed ring or rings that combination can take place in one position only, i.e., at the carbon atom in the alpha (first) position to the nitrogen of the nucleus. The structure of methyl benzthiazole ethiodide will serve as an illustration of the thiazole nucleus.



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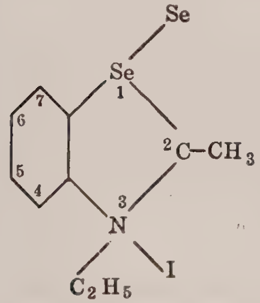
[31] *J. C. S.* (1931) 777.

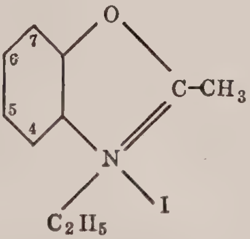
The symmetrical thiazoles consist of two thiazole nuclei with or without condensed rings connected by a methine group. The methyl group (or halogen) in the 2-position is the reactive part of the molecule in the condensation reaction by which the simple cyanines are formed.

The trinuclear cyanines of the thiazole type may be included in this class since the three nuclei are connected by two methine groups. A patient [32] assigned to Eastman Kodak Co. lists dyes of this class which contain three benzthazole, benzoxazole or selenazole nuclei respectively. They were obtained as by-products of the dinuclear cyanines. They are similar to neocyanine. The patent claims that these dyes increase the normal sensitivity of photographic emulsions, both as to intensity and range.

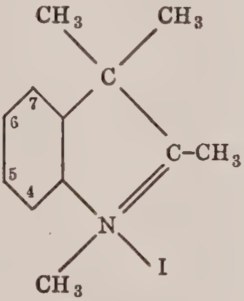
The symmetrical ozaxoles, selenazoles and indoles have the same structural configuration as the thiazoles. The following illustrations will show the structure of the various nuclei respectively:



2-methyl benzselenazole ethyl iodide



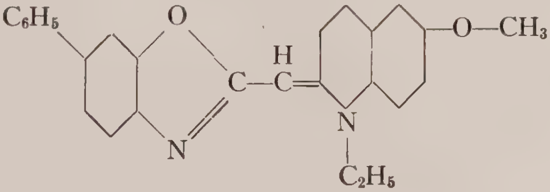
2-methyl benzoxazole ethyliodide



1,1,2 trimethyl-indolenine methiodide

I. Unsymmetrical Simple Cyanines

An example will serve to illustrate the structure of a typical unsymmetrical cyanine:



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[32] U.S.P. 2,108,845.

This is one of the very recently prepared unsymmetrical cyanines of the pseudo or *2,2′* class. It is prepared by condensing 5-phenyl-2 methyl-benzoxazole ethiodide and 6-methoxy-2-ethyl thiol-(-S-C H) quinoline ethiodide. The dye might be named 5-phenyl-2 ethyl-benzoxazoline-6 methoxy-2 ethyl-quinoline pseudocyanine.

II. The Carbocyanines

1. *From Quinoline or Pyridine nuclei* there are the 4:4′, 2:2′ and 2:4′ linkages corresponding to the originally named compounds of Kryptocyanine, Pinacyanol or Sensitol Red, and Dicyanine. Neocyanine is similar to Kryptocyanine except that the central carbon atom of the 3-carbon chain has its hydrogen replaced by a lepidine ethiodide residual nucleus. These are important dyes since they furnished the first panchromatic and the first infra-red sensitizers, and also furnish at the present time several important sensitizers.

2. *Symmetrical Carbocyanines* from the 5-membered ring-compounds. These compounds contain only one type of linkage, i.e., 2:2′ combination. In this class are found many of the best sensitizers for the yellow.

3. *Unsymmetrical Carbocyanines.* There are the same possibilities as to number of dyes in this class as is found in the unsymmetrical simple cyanines (q.v.). The first unsymmetrical carbocyanine dye was probably prepared about 1929 or 1930 [33] although as first prepared some of the symmetrical dyes of the two or more possible combinations were also formed. In some cases a complete or even partial separation of the dyes is not possible. New processes have been developed however by all firms producing unsymmetrical sensitizing dyes, which, it is claimed, prevent the formation of symmetrical dyes.

4. *Unsymmetrical Chain Substituted Carbocyanines.* In 1928, Miss Hamer of England prepared three thiocarbocyanines containing a methyl group [34] substituted on the central or meso carbon of the chain. It was observed that the sensitizing bands moved slightly to the short wave end of the spectrum, as compared to the normal carbon chain, thus partially filling the depression in the green. It was further observed that the intensity of sensitization was materially increased in the green and yellow.

Many representatives of this class have been prepared since 1928; the chief meso-substitutes are: CH_3, C_2H_5, C_3H_7 and $CH_2C_6H_5$, although the phenyl, nitrophenyl, furyl and other groups have been used.[35] This type of substituted compound coupled with those substituted in the rings has made these dyes very important intensive sensitizers for the red; there are also some good sensitizers for the orange, yellow and green in this class. The dyes from the benzthiazole nuclei yield a sensitivity, it is claimed, which is four to eight times higher than the old pinacyanol emulsions and at the same time have good stability and clarity.

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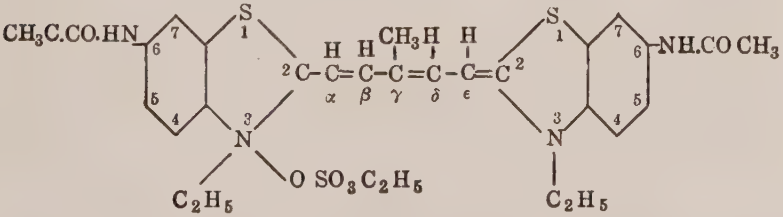
[33] D.R.P. 539,784 of 1929.

[34] Hamer, *J. C. S.* (1928) 3160.

There are symmetrical and unsymmetrical compounds of quinoline, pyridine and of the various 5-membered rings with or without condensed nuclei. The dyes of the thia condensed heterocyclic rings of the symmetrical type are used most generally, although the oxa and selena dyes of the same type have been used to some extent.

III. Polymethines

1. *Dicarbocyanines or Pentamethines.* They contain a 5-carbon chain with or without alkyl, aryl or other group substitutions in the chain. The substitutions may be on the different carbons of the chain. Examples of this type are given in a patent[36] assigned to the Agfa Ansco Co. If the five carbons of the chain are designated according to the Greek alphabet beginning at the quaternary nucleus, the substitutions of groups may be found on the α, β, γ, δ (delta), and ε carbon atoms. An example is:



The dye is named bis- [3-ethyl-6-acetylamino-benzthiazole-(2)]-γ-methyl pentamethine monoethylsulfate. A dye of this configuration has a maximum of absorption at about 670 mμ. The substituted β-ethoxyacrolein acetals are used as linking agents. There are symmetrical and unsymmetrical compounds of quinoline, of pyridine and of the various 5-membered rings with or without condensed nuclei. The most important compounds are those containing sulfur and selenium. Of the quinoline derivatives only the symmetrical 4:4′ compounds are mentioned.

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[35] U.S.P. 2,112,140 of 1938.

[36] U.S.P. 2,104,064.

2. *Tricarbocyanines or Heptamethines.* They contain a 7-carbon chain with or without substitutions on the carbon atoms of the chain. The substitutions are similar and in similar positions to those in the dicarbocyanine chain. Only the symmetrical nuclear thia-compounds seem to have been prepared and used. The unsubstituted and substituted glutaconaldehydes respectively are used for this class of cyanine. They are sensitizers for the range 650–1050 mμ. A patent [37] assigned to Agfa Ansco gives examples of thia tricarbocyanines containing a substituted chain. Intermediates were used which give an acetyl-oxy ($CH_3CO.O-$) group substituted for hydrogen in one of the seven methines of the chain.

3. *Tetra- and Pentacarbocyanines.* These dyes contain a carbon chain of nine and eleven carbon atoms respectively. A study of the previous classes of cyanines will show that there are almost an unlimited number of possible compounds in these two groups. However, the chief representatives which have been prepared are the symmetrical benzthiazole, selenazole and indole compounds containing various substitutions in the ring such as alkoxy, alkyl, aryl and naphthyl with an acetyl-oxy group in the carbon chain. The work of development of these polymethines is due almost entirely to W. König and his coworkers in Germany. The structural configurations ascribed to these dyes [38] were classed as probable. Examples of the structural configurations will be given under the preparation of cyanines.

Intermediates for the Cyanines.—The substances classed as direct intermediates or what are known as beginning materials for preparation of the actual cyanine dyes, may be divided into two classes, e.g. (1) cycloammonium salts and (2) linking agents for these salts.

1. *Cycloammonium salts.* The most commonly used are, (*a*) quinaldine ethiodide, (*b*) 2-methylbenzthiazole ethiodide, (*c*) 2-methylbenzselenazole ethiodide, (*d*) 2-methylbenzoxazole ethiodide, (*e*) 1, 2, 3, 3-tetramethyl indolenium iodide, (*f*) lepidine ethiodide. The structural formulas are as follows:

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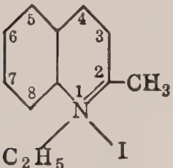
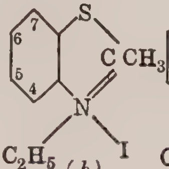
[37] U.S.P. 2,104,064 of 1938.

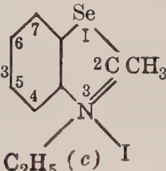
[38] U.S.P. 2,158,287 of 1939.



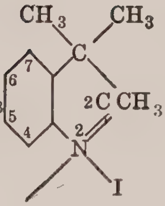
(a)



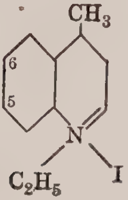
(b)



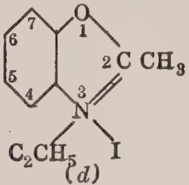
(c)



(e)

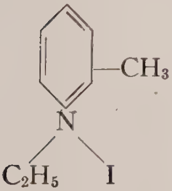


(f)

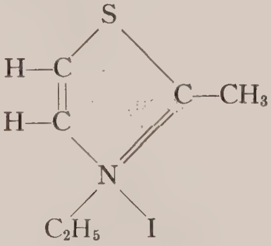


(d)

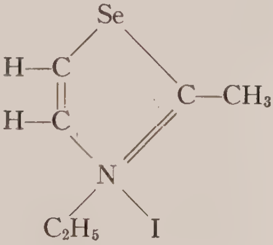
These compounds may be considered as derivatives of quinoline, benzthiazole, benzselenazole, benzoxazole, dimethyl indole or dimethylbenzpyrrole and quinoline respectively. The corresponding single ring compounds are used to some extent in the preparation of the cyanines but are not used as extensively as the condensed ring compounds, chiefly because the latter are better sensitizers than the corresponding single ring cyanines. The structures of the corresponding single membered ring compounds are:



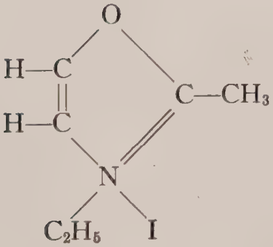
(a)



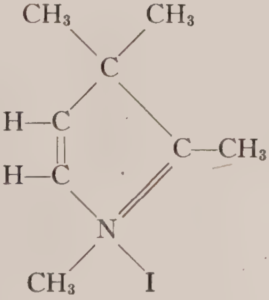
(b)



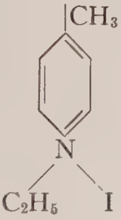
(c)



(d)



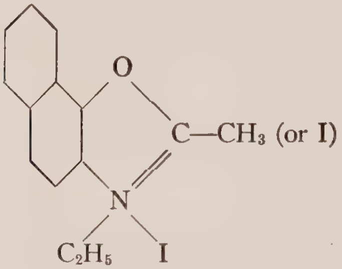
(e)



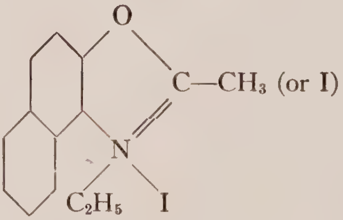
(f)

They are the ethiodides of (*a*) 2-methyl pyridine, (*b*) 2-methyl-thiazole, (*c*) 2-methyl-selenazole, (*d*) 2-methyl-oxazole, (*e*) 1, 2, 3, 3-tetramethyl pyrrole, and (*f*) 4-methyl pyridine. These compounds are considered as derivatives of pyridine, thiazole, selenazole, oxazole, 1, 1, 2-trimethyl pyrrole and pyridine respectively.

In addition to the one and two ring structures, there are the three ring compounds:

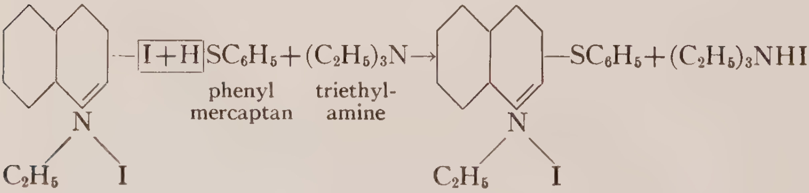


2-methyl-α-
naphthoxazole



2-methyl-β-
naphthoxazole

Most of the intermediates given as illustrations were known for sometime before any organized effort was made to prepare cyanines for photography. There have been very few compounds discovered since the chemistry of cyanines began to develop which have been used to prepare cyanines. These new compounds generally are not new structurally but modifications of old structures prepared by substitution of a more active group for a less active group or atom. An example is 2-phenyl thioquinoline ethiodide. It is prepared by treating 2-iodo quinoline ethiodide with a mercaptan such as phenyl mercaptan (thiophenol) in presence of triethylamine and absolute ethyl alcohol. The reaction is represented diagrammatically as follows:


I+H
SC$_6$H$_5$+(C$_2$H$_5$)$_3$N→
phenyl mercaptan
triethyl-amine
—SC$_6$H$_5$+(C$_2$H$_5$)$_3$NHI
N
C$_2$H$_5$
I
N
C$_2$H$_5$
I

2-iodo quinoline ethiodide

2-phenyl thiol quinoline ethiodide

The reactive group of this molecule is the arylthiol, the presence of which in certain intermediates has made it possible to prepare the cyanines which were previously known but as prepared by the older methods were of no value as sensitizers. The simple cyanines of the oxacyanines class are the best examples. This intermediate also permitted the preparation of the unsymmetrical simple cyanines, such as the oxathia, indoxa and indothia.

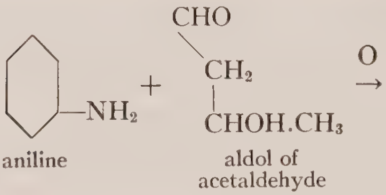
The greatest progress which has been made in the development of intermediates for cyanines has been along the lines of ring substitutions, i.e., replacements of hydrogen attached to ring carbons in the benzene and naphthalene nuclei attached to the respective heterocyclic nucleus.

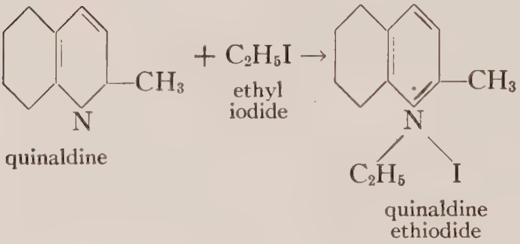
Ring Substitutions.—The groups which have been substituted into the respective rings are: alkyls, such as CH_3, C_2H_5 and C_3H_7; aryl and alkaryl, C_6H_5 and $C_6H_5CH_2$—; alkoxyl, such as $O—CH_3$ and $O—C_2H_5$; halogens; amino and substituted amino group; acetylamino or $NH\,CO\,CH_3$. If the system of numbering is employed as given in the illustrated structural configurations the quinoline nuclei are substituted in the 6- or 7-position, and the five numbered nuclei in the 5- and 6-positions. Halogens substituted into the ring tend in general to depress the intensity of and shift the spectral sensitiveness toward the red.

The object of the ring substitutions in general is to increase the intensity of sensitization. It is impossible to determine in advance the effect of ring substitutions even when the behavior of the corresponding symmetrical dye is known. For example, the substituted benzoxazole ring increases the intensity considerably, the substituted indol ring only a slight amount but the substituted unsymmetrical indo-oxocarbocyanine increases the intensity very markedly. It is understood here that the same group is used in each of the ring substitutions.

Preparation of Cycloammonium Salts.—These compounds are sometimes called quaternary salts. The following are examples:

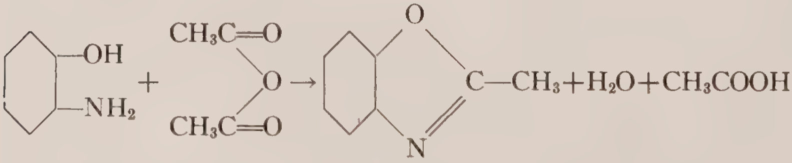
1. *Quinaldine or 2-methylquinoline ethiodide.* It is prepared by the interaction of the aldol of acetaldehyde, aniline, nitrobenzene and sulfuric acid (Doebner-Miller reaction):





2. *2-methyl-benzthiazole.* Aniline is treated with acetic anhydride to form acetanilide which is then treated with phosphorus pentasulfide to give the corresponding thioacetanilide. This compound is then oxidized by means of potassium ferrocyanide to give 2-methyl-benzthiazole. The ethiodide is obtained by refluxing with ethyl iodide.

3. *2-methyl-benoxazole.* Ortho aminophenol is treated with acetic anhydride which effects the condensation. The process of preparation of this compound is known as the method of Ladenburg.[39]



Quaternary Nitrogen.—The quaternary nitrogens are obtained by boiling the respective heterocyclic base with an alkyl halide, alkyl paratoluene sulfonate, dialkyl sulfate, alkyl perchlorate, hydroxyalkyl sulfate and alkyl nitrate. Those most commonly used are the ethyl iodide (or methyl iodide in case of the indole compounds), ethyl paratoluene sulfonate, diethyl sulfate, ethyl perchlorate, β-hydroxy-ethyl-iodide and ethyl nitrate. The structural formulas of 3 are given:

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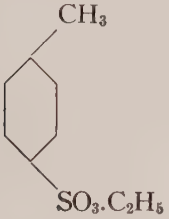
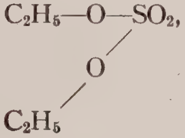
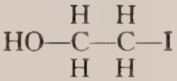
[39] *Ber.* **9** (1876) 1524.



ethyl para
toluene sulfonate



di ethyl
sulfate



$$HO-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-I$$

β-hydroxy-
ethyl iodide

The group attached to the quaternary nitrogen has very little influence on the intensity or range of spectral sensitivity. The use of the groups depends on the results desired. For example, a symmetrical dye is prepared as the alkyl paratoluene sulfonate which as such could not be recovered satisfactorily from the reaction mixture. It is changed to the ethiodide by treatment of the solution of dye as prepared with KI, in order to precipitate the dye. It is known also that the ethiodide is a better sensitizer than the corresponding ethyl paratoluene sulfonate.

Linking Agents

All true cyanine dyes are the result of the linking of two heterocyclic nuclei or rings by a methine (=CH—) group or a chain of methines. These linking groups are formed during the process of condensation either directly or by the stepwise method.

Simple Cyanines or Monomethines.—The linking agent for the monomethines, or simple cyanines, is an active methyl or CH_3 group, which is contained in one of the two heterocyclic nuclei used. For the quinocyanines, the CH_3 group must be in the alpha or gamma position to the nitrogen of the ring to be active. In case of the thio-, seleno-, oxy- or indolene compounds, the methyl group must be on the carbon atom between the respective elements S, Se, O or $=C(CH_3)_2$ and the nitrogen atom of the ring—e.g. the 2-position for the 5-membered rings.

Carbocyanines or Trimethines.—The first substance used as a linking agent was formaldehyde. It is of importance only because it was discovered in 1905 that by using this compound a new type of dye could be obtained. It was used as the linking agent in the preparation of all of the various carbocyanines up to about 1922. The orthoformic acid esters were discovered in 1922, and since then have been used very extensively.

There are many other substances used as linking agents for the carbocyanines, as shown by the patent literature. Some of these are: the ortho esters of propionic acid, *n*-butyric, *n*-valeric, *n*- and iso-caproic, phenylacetic, phenyloxyacetic and benzoic acid, tetraethyl orthocarbonic acid ester, diorthoformyl methylaminodiphenyl disulfide and diphenyl formamidine. It is believed that the use of ethyl orthoformate gives better results in most cases for the preparation of the carbocyanines than any of the other linking intermediates. For the ring substituted dyes the acetyl-methylene derivatives of one of the heterocyclic nuclei are used.

Dicarbocyanines or Pentamethines.—The most important linking agent for the preparation of the symmetrical pentamethines is beta-ethoxyacrolein acetal, and for the unsymmetrical dyes an alkyl substituted form of this compound is generally used. It was probably used as the first linking agent in the preparation of cyanines of this class. The preparation of the dye was based on the ideas contributed by König.[40] Kendall (B.P. 390,808) used an acetal of propargyl aldehyde to prepare dicarbocyanines.

Tricarbocyanines or Heptamethines.—One of the linking agents for the dyes of this class is glutaconaldehyde, dianil hydrochloride and what is described in the literature as the free form of glutaconaldehyde which is formed by the action of NaOH solution, on 2,4-dinitrophenyl-pyridinium chloride. The tricarbocyanines were discovered independently by three groups of workers of whom Wahl in Germany was the first (D.R.P. 499,967 of 1928). Miss Hamer of England (B.P. 351,555 of 1930; 354,826 of 1930) and Piggott and Rodd of England (B.P. 355,693 of 1930) also prepared tricarbocyanines using this linking agent. The work of all three groups is based first, on the work of Zincke and his co-workers in Germany about 1904–1905, who showed that the pyridine ring of 2,4-dinitrophenyl-pyridinium chloride may be broken open in the usual manner, to give 2,4-dinitroaniline and presumably the enolic form of glutaconaldehyde and second, on the "displacement process" of König.

There have been several new linking agents for the heptamethines prepared and used quite recently, many of which are dyes although unsatisfactory as sensitizers. Most of these intermediates give methyl or acetyloxy substituted chains in the finished dyes. Examples with the probable structural formulas are: (1) ϵ-phenylimido-α-phenylamino-

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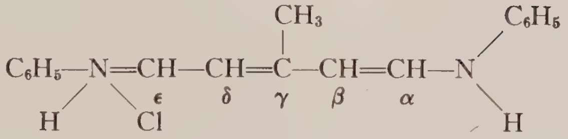
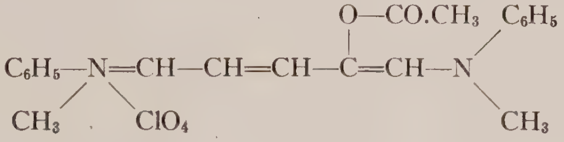
[40] König, *J. prakt. Chem.* (2), **86** (1912) 173.

(γ-methyl-α, γ-pentadiene)-hydrochloride,



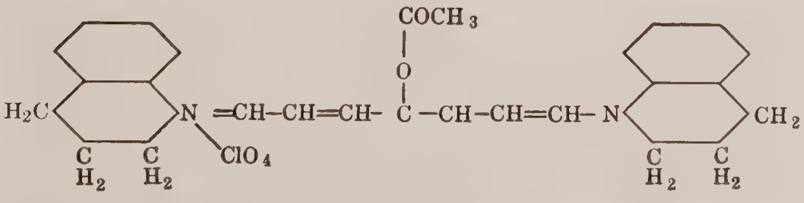
(2) δ-methyl phenylimido-α-methyl phenylamino-(β-acetyloxy-α, γ-pentadiene)-perchlorate,



The latter is prepared by condensing furfurol, monomethylaniline and a perchlorate with acetic anhydride. Substituted glutoconaldehydes are also used for the chain substituted dyes of recent discovery.

Tetra- and Pentacarbocyanines or Nona- and Undecamethines.—The linking agent first used for the nonamethines is the residue of 4-acetoxy-Δ 3, 5-heptadiene-1, 7-dial di-tetrahydroquinonolide perchlorate; its preparation is believed to be chiefly the result of the researches[41] of W. König, and others in Germany. The linking agent first used for the undecamethines, or pentacarbocyanines, is 4-acetoxy-Δ 3, 5, 7-nonatriene-1, 9-dial di-tetrahydroquinalide perchlorate.

More recently the azomethine compounds have been prepared and used for both the tetra- and pentacarbocyanines. An example is the acetyloxy heptamethine azo compound of tetra- hydroquinoline perchlorate:



The imido-amino acetyloxy substituted dienes, similar to the example given under heptamethines, may also be used for both the tetra- and pentacarbocyanines. There are many different combinations which have been suggested recently but the examples given are sufficient to illustrate this class of compounds.

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[41] *Ber.* **67** (1934) 1274.

PREPARATION OF THE CYANINES

The fundamental conceptions developed in the realm of free research have contributed very much to the development of the cyanine dyes. Examples are the syntheses of Skraup and of Döbner and von Miller about 1885 in the quinoline series; the work of Kaufman and Vonderwahl about 1912 on the constitution of the monomethines, and that of Zincke and his associates about 1904 on the rupturing of the pyridine nucleus which made possible the development of the tricarbocyanines. However, most of the work in the development and preparation of the cyanine dyes has been carried out in the laboratories of the photographic industry.

Probably the most outstanding research work in the development of the actual sensitizers was carried out by Mills and Hamer[42] about 1920, when they proved the structure of Pinacyanol (M.L.B.) or Sensitol Red (Ilford)and, therefore, settled the question of the constitution of the chain cyanines.

Simple Cyanines.—In this group are the lepidine-cyanines (cyanines), isocyanines and pseudo or ψ-cyanines, the symmetrical heterocyclic cyanines of the five-membered rings with or without condensed nuclei, and also substituted condensed and uncondensed nuclei, and the *unsymmetrical* cyanines of the many possible combinations using quinoline, or pyridine, and the various heterocyclic five-membered ring compounds. Only a brief resume is given for the preparation of the dyes of this class. Cain and Thorpe in *The Synthetic Dyestuffs and Intermediate Products,* 1933, give the methods of preparation which were used up to 1925–30. Since then new methods have been introduced which give better yields although fundamentally the new methods are not much different than the older.

The preparation of the simple cyanines consists in the condensing of two heterocyclic nuclei, with or without condensed rings, and containing nitrogen, one of which contains a reactive methyl group and a reactive halogen (chiefly iodine), a reactive hydrogen or thiol group such as —SC_6H_5 in the presence of a basic condensing agent. A reactive group in the quinoline and pyridine derivatives must be in the 2- or 4- (α or γ) positions relative to the nuclear nitrogen and attached to a carbon atom. In the five-membered ring derivatives the reactive group is in the 2- or α-position relative to the nuclear nitrogen and also attached to a carbon atom.

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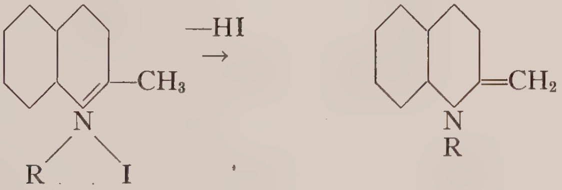
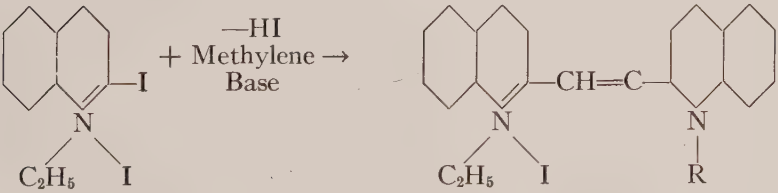
[42] *J. C. S.* 117 (1920) 1550–1562.

Condensing Agents for Simple Cyanines.—In the preparation of the earlier monomethines potassium or sodium hydroxide in alcoholic solution was generally used. These have been displaced to a considerable extent by the strong organic bases such as: triethylamine, trimethylamine, piperidine, triethanolamine, N-butylamine, diethylamine, alkylaminoalcohols, and guanidine carbonate. These organic bases are generally used with pyridine as a solvent for the dye intermediates. In some cases pyridine acts as a condensing agent. Recently [43] anhydrous potassium carbonate in absolute ethyl alcohol has been proposed as a condensing agent; it is also a binding agent for the acid produced in the condensation process. In general, however, triethylamine seems to have proved the best condensing agent for the monomethines. It is believed that the mechanism of the reaction in the preparation of the dye consists in the removal of acid (HX) from the cycloammonium salt to give a free but unstable methylene base which unites with a second molecule of a salt to form the dye. The following diagrams will illustrate the preparation of a pseudocyanine,



cycloammonium salt

methylene base (unstable)



2-iodo quinoline ethyl iodide

monomethine dye

This method is generally used for the preparation of the symmetrical cyanines of this class using all of the various possible combinations. However, it has been discovered within the last 10 to 12 years that symmetrical 2,2′ and also 2,4′ monomethines are prepared with better yields and in a purer form if the alkyl thiols are used in place of iodine. This applies particularly to the 5-membered nuclei containing the benzene or naphthalene ring structure. The alkyl thiols are prepared by condensing a thioether or aryl mercaptan with a quaternary salt having a reactive methyl, or halogen, to form, for example, a 2-ethylthiol of benzselenazole ethiodide with the general formula of:

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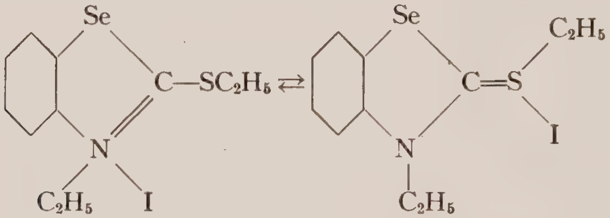
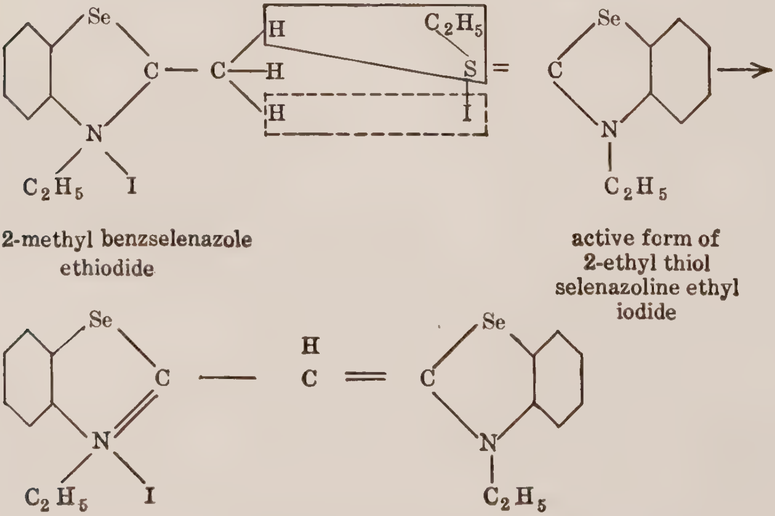
[43] U.S.P. 2,120,322 of 1938.



probably the active form

The alkyl thiols are said to possess an unusual reactivity with active methyl groups. The reaction proceeds diagrammatically as follows to form a 2,2′ cyanine:



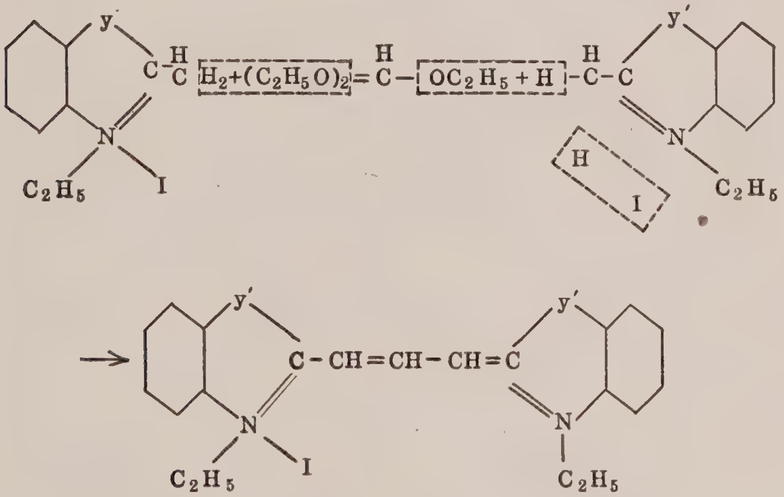
2-methyl benzselenazole ethiodide

active form of 2-ethyl thiol selenazoline ethyl iodide

3,3′ diethyl-2,2′-benzselenazoline iodide

This is a good sensitizer for the green and yellow, being many times more energetic as a sensitizer than erythrosine. However, ring substituted compounds of other nuclei are said to be even more active sensitizers for the green and yellow than this selenapseudocyanine.

Carbocyanines or Trimethines.—The patent literature indicates that the carbocyanines are the most numerous of all the cyanines. Mills and Pope in an article in the Photographic Journal of 1920 have given methods for the preparation of about eighteen different dyes. Formaldehyde was used as the linking agent and sodium or potassium hydroxide as the condensing agent. Since the use of orthoformic acid ester has supplanted the formaldehyde method, the following diagram using ethyl orthoformate will be used as an illustration of the preparation of a carbocyanine with pyridine as the most generally used solvent, although acetic anhydride is used as a solvent in case of the oxazole derivatives.

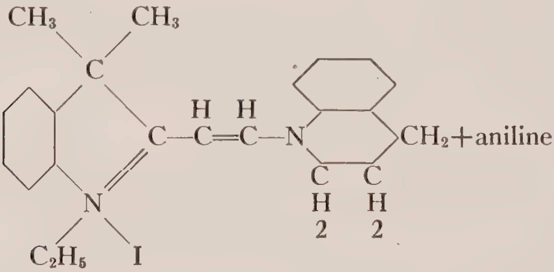


where y = $—CH=CH—$, $—S—$, $—Se—$, $—O—$, or $—C(CH_3)_2—$; y′ may or may not be the same as y. The first dye of technical importance in this group was Pinacyanol which, however, has largely been replaced by other dyes.

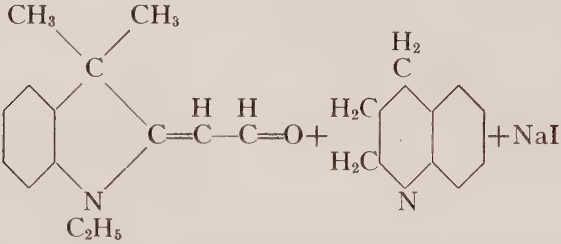
The greatest number of new cyanine dyes, new processes and improvements in old process have occurred in the field of the carbocyanines, the most important development being the preparation of unsymmetrical dyes of all kinds and classes of carbocyanines, of higher activity than any so far known of this class.

The unsymmetrical dyes have been prepared by condensing a ring heterocyclic nucleus containing an active aldehyde group with a quaternary salt of heterocyclic rings having a reactive methyl group.

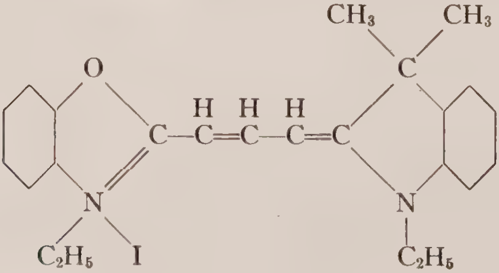
Symmetrical dyes of this class may also be prepared by this method. The active, or so-called ω-aldehyde, is prepared by a rather complicated process which consists in first preparing an amidine by condensing formylaniline and tetrahydroquinoline in presence of phosphorus trichloride. The amidine so formed is then condensed with a quaternary salt of a heterocyclic nuclei by means of acetic anhydride to form a compound of the formula:



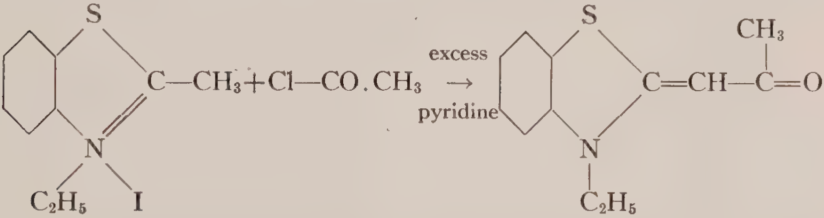
This compound is then treated with NaOH to give the ω-aldehyde:



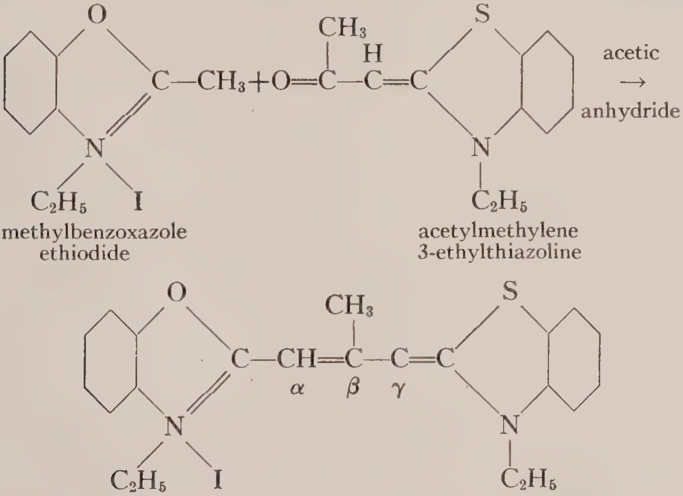
The aldehyde so named is then condensed for example with 2-methylbenzoxazole ethiodide, by means of acetic anhydride, to give an unsymmetrical dye which is said to be a highly active sensitizer or what is known as a supersensitizer. The reaction product so formed is:



These processes were originally developed largely in Germany. To obtain a substituted chain compound ethyl ortho esters have been used. However another commonly used method of preparation for the substituted chain carbocyanines is by the condensation of an acetyl methylene derivative[44] of a quaternary salt of a heterocyclic nuclei containing an active methyl group in presence of an acid condensing agent. The acetyl methylene compound is obtained diagrammatically as follows:



This ketonic compound is then condensed with a quaternary salt by means of acetic anhydride to give a chain substituted dye of the symmetrical or unsymmetrical type with or without ring substitutions. An example of an unsymmetrical dye is as follows:



2-methylbenzoxazole ethiodide

acetylmethylene 3-ethylthiazoline

β methyl-2:2′ diethyl α, γ-benzoxazol-benzothiacarbocyanine iodide.

Dicarbocyanines or the Pentamethines.—The dicarbocyanines are not considered as important as the tri-, tetra- and pentacarbocyanines. The most important method of preparing these compounds is by the condensation of two cycloammonium salt molecules with one molecule of beta-ethoxyacrolein-acetal. As may be expected, the reactions are very complex and since these dyes are of only minor importance the method of preparation will not be given.[45] The sulfur dyes of this class are probably the most important. A typical dicarbocyanine of the unsubstituted type is:

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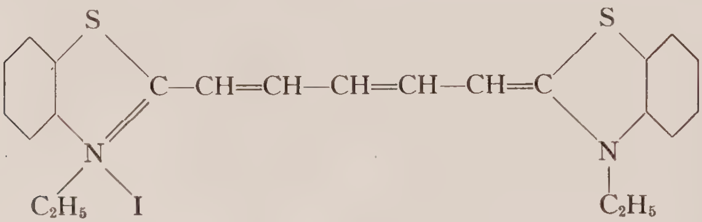
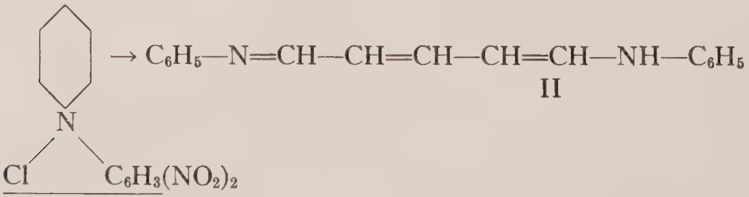
[44] Brooker and White, U.S.P. 2,112,139 of 1938.



The dyes of this class are sensitizers for the red and infra-red.

Tricarbocyanines or Heptamethines.—The most important direct intermediate in this class is glutaconaldehyde in the form of its dianil hydrochloride. The development of the dyes of this class is based largely on the work of Zincke and the "displacement process" suggested by König. Zincke and his co-workers showed that the pyridine ring of 2,4-dinitrophenyl-pyridinium chloride (I) may be broken open by treating with NaOH to give the dianil of glutaconaldehyde. This substance (II) which is classed by König as a streptopolymethine dye is then subjected to the "displacement process" of König by condensing with two cycloammonium salt molecules in absolute alcohol in presence of sodium ethoxide to produce a tricarbocyanine dye. The "displacement process" of König[46] consists in the replacements of a $C_6H_5N=$ and a $C_6H_5NH—$ by the cycloammonium salt residues. The formulas and processes are represented diagrammatically as follows:



$$\rightarrow C_6H_5—N=CH—CH=CH—CH=CH—NH—C_6H_5$$

II

(1)

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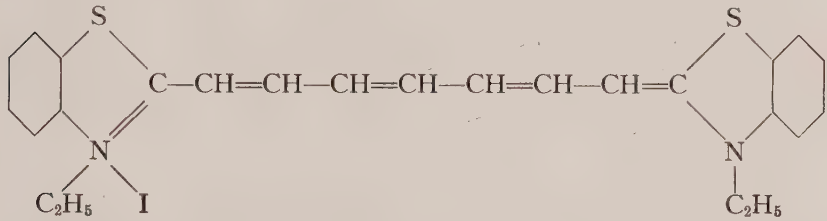
[45] For the chain substituted dyes of this class, see U.S.P. 2,104,064.

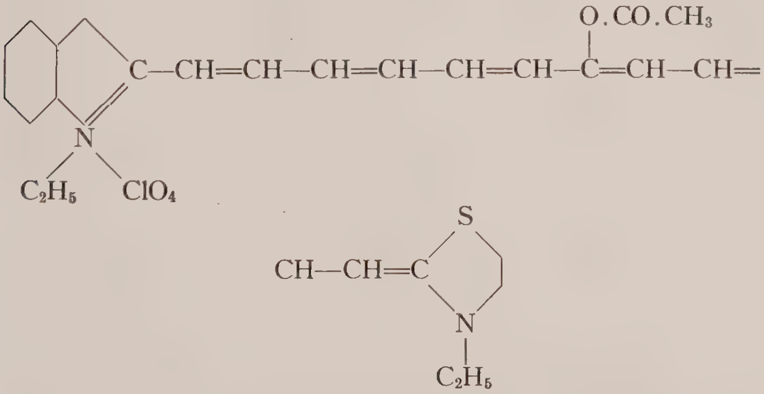
[46] Konig, *J. prakt. Chem.* (2), **86** (1912) 173.

Formula (II) or a streptopolymethine is condensed with two molecules of I-methyl-benzthiazole-ethyl iodide to give the dye 2,2-diethyl benzthiotricarbocyanine iodide the structural formula of which is:



For the preparation of the chain substituted heptamethines the alkyl substituted pentadienes of the imido-amino type are used. Such substances as sodium ethylate containing a little free sodium are used as condensing agents. The method of W. König[47] involving his unique "displacement process" may also be employed to prepare heptamethines containing the oxyacyl group in the chain.

Tetra- and Pentacarbocyanines or the Nona- and Undecamethines.—These dyes are sensitizers for the extreme infra-red. The preparation of these dyes is the result of the work of König[48] and others in Germany based on König's "displacement process" of 1912. A typical formula, of a pentacarbocyanine dye, is:



For methods of preparation of these long chain compounds the student is referred particularly to the patent literature.[49] These dyes are very unstable because of the presence of the oxyacyl groups since the molecule tends to split at these groups. The oxyacyl groups also tend to lower the intensity of sensitization.[50]

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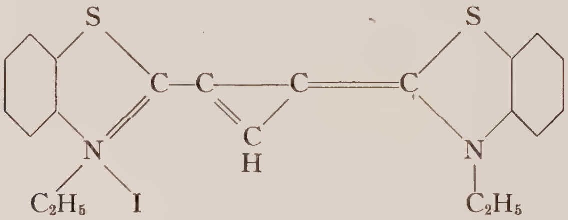
[47] W. König, U.S.P. 2,158,287 of 1939.

[48] *Ber.* **67** (1934) 1274.

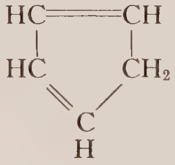
[49] König, U.S.P. 2,158,187 of 1939.

Symmetrical tetra- and pentacarbocyanines are said to have been prepared in Germany which do not contain chain substitutions.[51] They are said to be more stable and have greater intensity [52] of sensitization than the corresponding acetyl oxy chain substitutions. In general, however, only a few of these long chain cyanines have found any practical use.

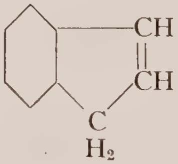
Cyanines with Cycloparaffins Linkages.—In recent years new dyes of the cyanine type have been prepared in England and Germany containing the cyclodienes as the linking agents for the quaternary nitrogen and the ternary nitrogen heterocyclic bases. An example is given from the patent literature: [53]



Other cyclodienes said to have been used are cyclopentadiene and indene. The structural formulas are:



cyclopentadiene



indene

Merocyanines

Definition and History.—The merocyanines are dyes which are formed as the result of a condensation of a heterocyclic nuclear compound containing a reactive methylene group and quaternary heterocyclic nuclear salt. A reactive methylene (CH_2) group is one which is adjacent to a nuclear carbonyl or thione group. The sensitizing system is:

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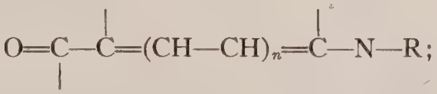
[50] Dieterle and Leh, *Z. wiss. Phot.* **34** (1935) 249.

[51] Dieterle and Riester, *Z. wiss. Phot.* **36** (1937) 68–72 and **141–44.**

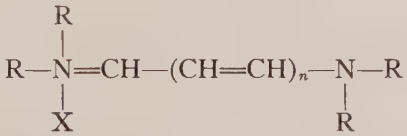
[52] *Luft. Photowoche* 1936, 440.

[53] Gevaert Photo-Producten, B.P. 511,940 of 1936.



$$\mathrm{O{=}\underset{|}{C}{-}\overset{|}{C}{=}(CH{-}CH)_{\mathit{n}}{=}\overset{|}{C}{-}N{-}R};$$

where n is zero or a position integer and R is hydrogen, alkyl or aryl. This illustration is not intended to indicate that systems of this type exist as straight chain compounds; such systems are found only in heterocyclic nuclear structures. Comparison with the cyanine system shows there is a close relationship between the two systems. The cyanine sensitizing system is;



$$\mathrm{R{-}\overset{\overset{R}{|}}{\underset{\underset{X}{|}}{N}}{=}CH{-}(CH{=}CH)_{\mathit{n}}{-}\underset{\underset{R}{|}}{N}{-}R}$$

where X is halogen, chlorate, alkosulfate, paratoluene sulfonate or nitrate, n is zero or a positive integer. R is hydrogen, alkyl, aryl or alkaryl.

The merocyanines are of comparatively recent origin; Kendall of Ilford and Brooker of Eastman Kodak having discovered these independently. The first mention of the name merocyanine occurs in a French patent [54] which describes a dye which is prepared by the condensation of 1-acetyl methylene-3-ethylbenzthiazoline ethiodide with 3-ethylrhodanine. However, the first patents in England to mention the condensation of similar intermediates and use of similar dyes are B.P. 426,718; B.P. 428,222; B.P. 428,359 and B.P. 428,360, all issued to James D. Kendall of England.

The first patent in the U.S.A. to mention merocyanines is U.S.P. 2,161,331 of 1939 application 1935 by Brooker and Van Dyke.

Classification of Merocyanines.—Merocyanines are classified in about the same way as the cyanines, namely, Merocyanines, Merocarbocyanines and Meropolycarbocyanines. The naming of the dyes depends on the method of numbering the atoms in the heterocyclic ketonic nucleus. For this discussion the rhodanine type of intermediate will be numbered as follows: the reactive methylene group is number 1, and the ketonic carbon 2. Rhodanine is taken as an example:

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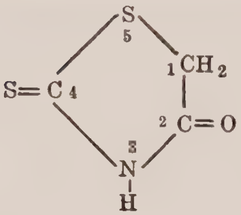
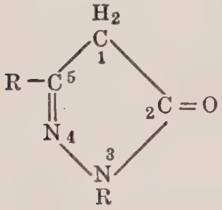
[54] Kodak Pathé, F.P. 808,598.



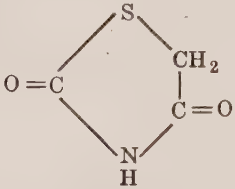
Rhodanine

Intermediates.—They are the methylene-ketonic heterocyclic compounds, quaternary or cycloammonium salts and linking agents.

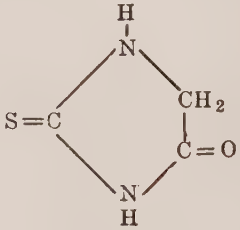
There are a large number of methylene-ketonic compounds available. The more commonly used in addition to rhodanine are: the alkyl and aryl derivatives of rhodanine, such as methyl, ethyl and ethylphenyl. These groups replace the hydrogen of the ternary nitrogen. Other important type compounds are:



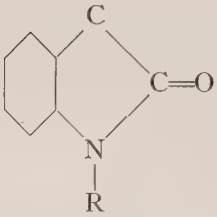
Pyrazolones



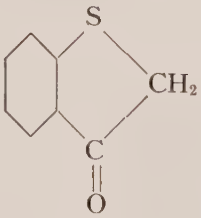
2:4 Diketotetrahydro thiazole



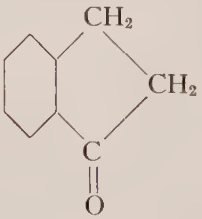
Thiohydantoin



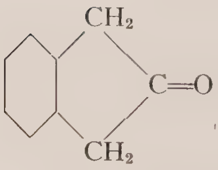
oxyindoles



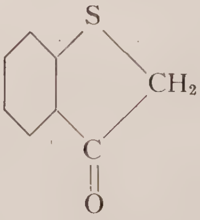
thioindoxyl



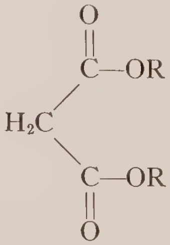
α-hydrindone



β-hydrindone

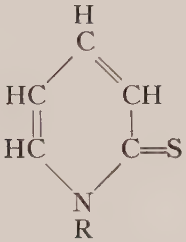


thionaphthenone

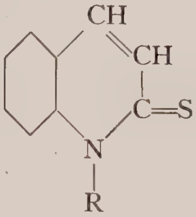


malonic ester

By analogy it would be anticipated that the ketonic oxygen can be replaced by sulfur thus giving the thione compounds. Examples are:

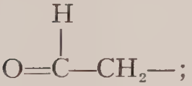


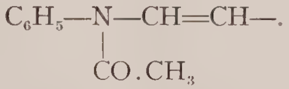
alkyldihydro-pyridine-2-thione



alkyl dihydro-quinoline-2-thione

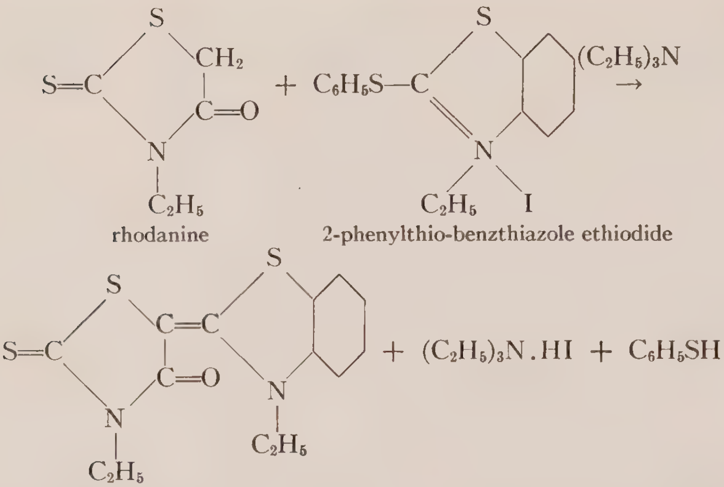
Quaternary Salts and Linking Agents.—For the quaternary salts most of those used in the cyanines theoretically could be used for the merocyanines. In practice the quaternary salt is condensed in the usual manner described under cyanines, which gives heterocyclic nuclei containing such active groups as, alkyl or aryl mercaptans or thiols, R—S—; acetylmethylene, $O{-}CCH_3.CH{-}$; formyl methylene,


$O{=}\overset{\overset{H}{|}}{C}{-}CH_2{-}$; acetanilidovinyl,


$C_6H_5{-}\underset{\underset{CO.CH_3}{|}}{N}{-}CH{=}CH{-}$. The thiols are formed by condensing the iodo heterocyclic nuclear compounds with a mercaptan or thio ether with the aid of triethylamine. The acylmethylene compounds use acyl halides with pyridine as the condensing agent and the acetyanilidovinyl with a strong organic base such as triethylamine.

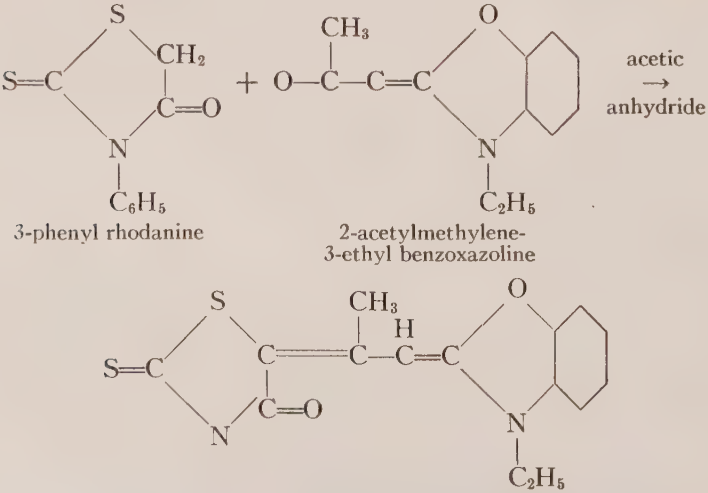
Preparation of Merocyanines.—

1. *The simple merocyanines* are prepared by condensing a keto-methylene compound with a quaternary salt of a heterocyclic nucleus using pyridine or triethylamine as a condensing agent. The reaction takes place diagrammatically as follows:


rhodanine
2-phenylthio-benzthiazole ethiodide
$(C_2H_5)_3N$
$+ (C_2H_5)_3N.HI + C_6H_5SH$

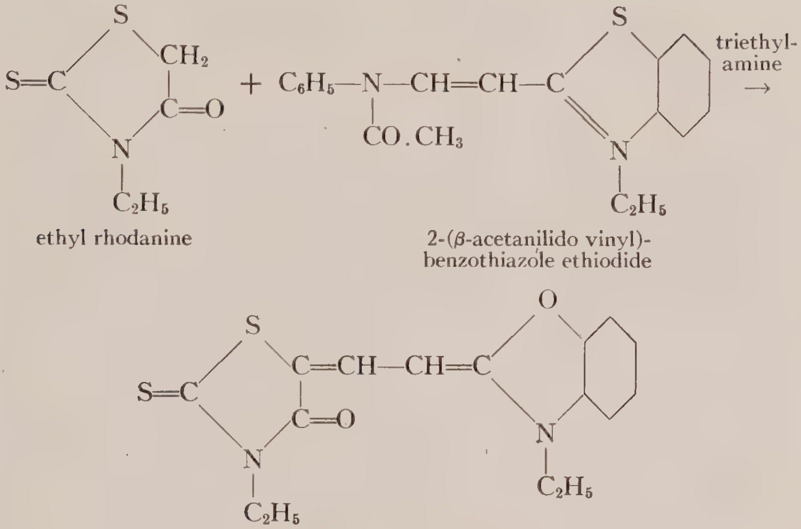
The corresponding iodo compound can be used in place of the phenylthio compound. Rhodanine can be replaced by one of the many keto-methylene or thione-methylene compounds.

2. *Merocarbocyanines.* For this class the acetylmethylene alkyl heterocyclic nitrogen nuclear compounds are condensed with the keto-methylene or thione-methylene compounds using acetic anhydride as a condensing agent or the acetanilidovinyl derivatives of a quaternary heterocyclic salt are condensed with the keto-methylene compounds to give a merocarbocyanine. An example of the first type of reaction is:



β-(3-ethyl-2-benzoxazolidene-ethylidene)-
α-methyl-3-phenyl rhodanine

An example of the second type of reaction is:



ethyl rhodanine

2-(β-acetanilido vinyl)-
benzothiazole ethiodide

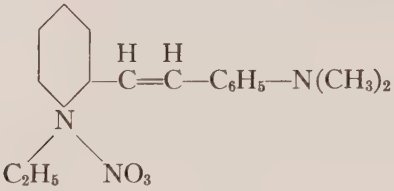
β (3-ethyl-2-benzothiazolinylidene-ethylidene)-
3-ethyl rhodanine

3. *Meropolycarbocyanines.* The methods employed in preparing the longer chain compounds are about the same as for the polymethine cyanines. The merotricarbocyanines have been prepared by about the same methods as given for the Tricarbocyanines using an ω-anilino-glutaconic anil hydrochloride.

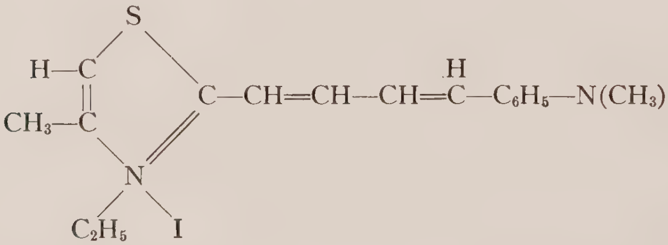
Sensitizing Properties of Merocyanines.—In general these dyes cover the visible spectrum, near infra and also infra-red. Little can be said at this time in regard to the intensity of sensitization of these compounds as compared to the corresponding true cyanines. However, the patent literature generally makes the claim that many of the dyes in this class impart a high degree of sensitivity to photographic emulsions.

THE PINAFLAVOLS

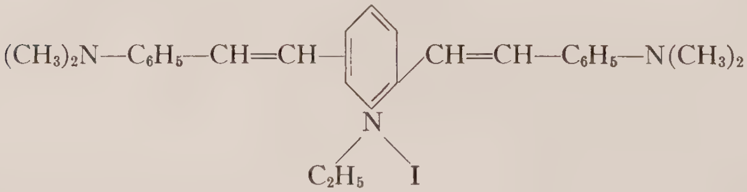
The pinaflavol class are sometimes called the Styryl dyestuffs. These dyes are prepared by condensing quaternary salts of heterocyclic nitrogen bases with aromatic aldehydes. The first commercial representative of the styryl or pinaflavol dyes was "Pinaflavol." It was first prepared in Germany in 1920 by condensing a quaternary salt of 2-methyl pyridine (α-Picoline) with *p*-dimethylaminobenzaldehyde; it is:



There are a great many possibilities in this group of dyes since there are many available aldehydes and quaternary bases. The pinaflavol from *p*-dimethylamino cinnamic aldehyde and 4-methyl thiazole ethiodide is said to be a strong sensitizer. It is represented by the following structure:



The distyryl dyes are of interest since they are said to be good panchromatic sensitizers of medium red but very high green sensitivity. An example is the formation of a distyryl compound by the condensation of two mols of an aromatic aldehyde with 2,6-dimethyl pyridine ethiodide which contains two reactive methyl groups:



Block and Hamer of England have given a review [55] of the development of this series of dyes up to 1930.

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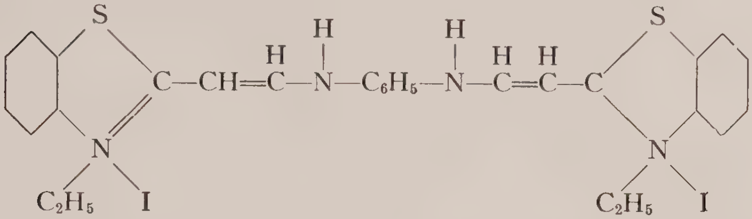
[55] *Phot. J.* **70** (1930) 374–390.

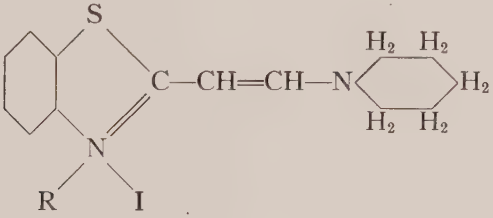
The Oxonols

Dyes from diamines may be classed as oxonols; example is:



Dyes of this type are said to be intensive sensitizers for silver chloride.[56] Several examples are given in the recent patent literature of this type using piperazine as the diamine.[57] Many of the intermediates are similar to those used for the preparation of the cyanines. Acetals of ω-aldehydes are used with the diamine compounds.

The hemioxonols are similar to the oxonols except that they are half oxonols. A typical formula is:



The piperidyl ($C_5H_{10}N$—) group may be replaced by such groups as 4-morpholyl, a 6-membered saturated nucleus containing oxygen para to the nitrogen, butylamino, diallylamino, di-tetrahydrofurfuryamino, and diethylamino. The linking agents are similar to those used in the true cyanines, thus there may be different length chains, substituted and unsubstituted.

The hemioxonols are said to be excellent sensitizers for silver chloride. The keto methylene compounds such as rhodanine may be used in place of the benzothiazole type of compound.

[56] I. G. Farben, F.P. 811,990 of 1936.

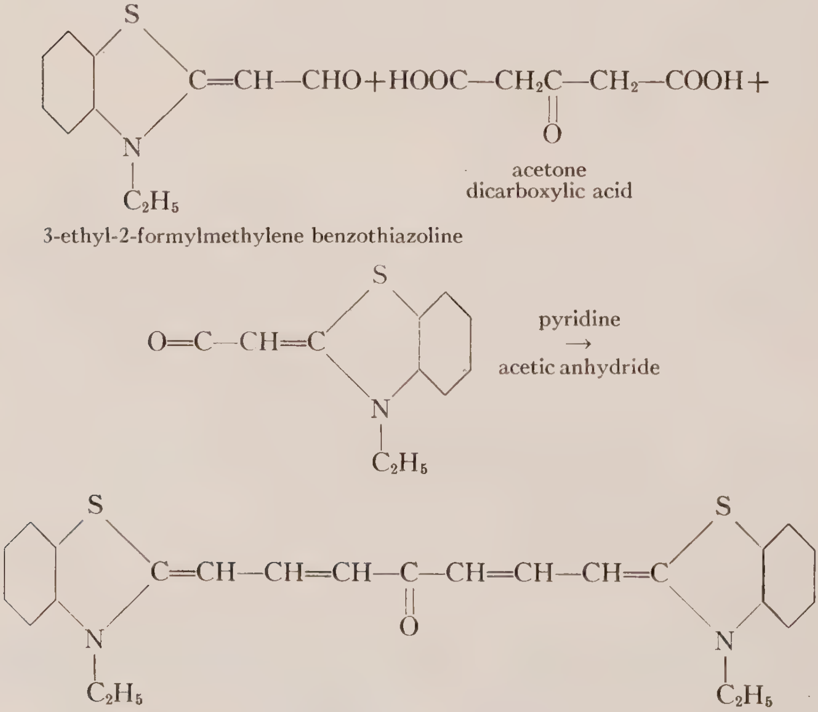
[57] White and Keyes, U.S.P. 2,166,736 of 1939.

Basic Di- and Triphenylmethanes

In this class are auramine, ethylviolet, methylviolet and magenta. These dyes were used as sensitizers before the turn of this century but have not been used to any extent since the cyanines were first put on the market.

Ketonic Acid, Cyano and Imino Cyanines

Ketonic Acid Dyes.—These dyes are very closely related to the cyanine dyes; in some cases the only difference is in the introduction of a carbonyl group in the linking chain. These compounds are condensed with two mols of a substituted aldehyde containing nitrogen in presence of acetic anhydride. The nitrogen may be attached to an aromatic ring or form part of a heterocyclic ring.

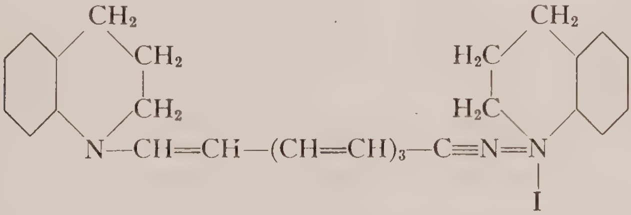

S
C=CH—CHO+HOOC—CH₂C—CH₂—COOH+
O
N
C₂H₅
acetone dicarboxylic acid
3-ethyl-2-formylmethylene benzothiazoline
S
O=C—CH=C
N
C₂H₅
pyridine
→
acetic anhydride
S
C=CH—CH=CH—C—CH=CH—CH=C
O
S
N
C₂H₅
N
C₂H₅

In the above reaction carbon dioxide and water are formed. In this type of compound the methine chain is broken by a carbonyl group.

Careful examination of the compounds used and the structural relationship of the finished dye indicates that it should be possible to produce a great variety of compounds. If the uncondensed 5-membered ring bases are used, it is claimed in the patent literature [58] that a sensitizer for the blue-green is obtained. It is possible with this class to include the whole spectral region from blue-green to the infra-red. Compounds of this type containing 15 carbon atoms have been prepared.

Cyano Cyanines.—These dyes [59] contain a cyano-keto type compound condensed with a heterocyclic nitrogen compound of the type used in cyanine dyes. The cyano compounds used may be represented by benzoylacetonitrile, $C_6H_5.–CH_2–CN$. These type compounds are condensed with such compounds as 1-(B-anilino-vinyl)-benzoxazole ethiodide in the presence of triethyl amine, to form a compound named α-(3-ethyl-2-benzoxazylidene-ethylidene)-benzoylacetonitrile. Little has been published of the sensitizing characteristics of this type of dye.

Imino-cyanines.—An example of this is an imino-nonamethine [60] prepared by condensing glutaconic acid with an unsaturated aldehyde of the general formula: $R.R_2 = N–CH = CH–CHO$ by means of an acid condensing agent such as acetic anhydride. In this aldehyde, R_1 and R_2 together form part of a heterocyclic ring, or are respectively an alkyl and an aryl group. More definitely R_1 and R_2 in the patent cited constitute a tetrahydroquinoline dihydro-α-methylindole or α-methylphenmorpholine residue. A typical nonamethine is:



It is claimed that this dye is a sensitizer for the infra-red but its stability is not given.

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[58] Riester, *D. Anm. I.* 57303 IVa/22e; F.P. 834,718 of 1938.

[59] Brooker, U.S.P. 2,153,169 of 1939.

[60] I. G. Farben, A.G.B.P. 512,470 of 1940.

CHAPTER IX

THE LATENT PHOTOGRAPHIC IMAGE AND ITS DEVELOPMENT

The Latent Photographic Image.—When light of a proper wave length falls upon a photographic emulsion some of the grains, the number depending upon the exposure, are so altered that they can be reduced to metallic silver by certain chemical reducing agents or "developers," while the grains which are not sufficiently altered by the incident radiation are not reduced.[1] The grains of silver halide thus altered, or rendered developable, form what is known as the latent photographic image.

The latent image cannot be extracted by chemical means, nor is any change visible at the highest powers of the microscope; developability is the only positive means of detection. It is nevertheless quite stable in the case of negative materials but relatively instable in the case of low speed materials particularly developing papers and to a lesser degree motion picture positive film. Numerous cases have been reported in the literature of the successful development of negatives ten, twenty and even thirty years after exposure. The stability of the latent image appears to depend to some extent on the character of the emulsion but more particularly upon the temperature, the humidity and absence of fog-producing substances, either in the packing or the atmosphere. With papers and positive film on the other hand, the fading of the image appears to begin very shortly, if not immediately after exposure and is a matter of only a few days or weeks at the most.

With high speed panchromatic negative materials [2] the latent image grows for a period of several months, then remains very nearly constant for a much longer period before fading begins. The increase in speed in the months following an exposure is most in evidence with panchromatic materials, in which case it may amount to as much as 200% within a year; is much less in high-speed, blue sensitive materials, and is not found at all on low-speed materials such as positive motion picture film. The growth in the latent image during this period appears to be confined to the lower densities; in the higher densities the increase is either proportionally less or there is frequently a lessening of loss in density. As a result, the shape of the *D*log*E* curve is changed, the period of decreasing gradient beginning at a lower density and comprising a larger part of the curve.

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[1] Latent images, i.e., the developable state, may be produced by pressure, by oxidizing agents, and by heat as well as by light. Russel, *Phot. J.* **39** (1899) 345. Clark, *Brit. J. Phot.* **70** (1923) 717. Wightman, *Brit. J. Phot.* **74** (1927) 447.

[2] Mees, *Photography and Focus* **39** (1915) 338. Jausseran, *Revue d'Optique* **8** (1929) 119. Heisenberg, Die Veränderung des latenten Bildes in Halogensilbergelatineschichten bei der Lagerung. *Veröff. des wiss. Zentral-Lab. Agfa.* Leipzig (1933) p. 47. Famulener & Loessel, *J. Soc. Mot. Pict. Eng.* **36** (1941) 374.

The graininess of the image appears to increase with the time elapsing between exposure and development and is independent of the growth, or fading, of the latent image.

If the exposure required to produce developability is greatly increased, a visible image is formed. This image consists of metallic silver, and it has been well established by studies with the microbalance, and from x-ray powder diagrams, that the products of the visible decomposition of silver halide are metallic silver and halogen.

Eggert and Noddack, who investigated the photochemical equivalence for the direct reduction of silver bromide by light, concluded that the photo-equivalence law of Einstein applies; in other words, each absorbed quantum results in the decomposition of one molecule of silver bromide producing one atom of silver and one of bromide.

There are many points of correspondence between the latent photographic image and the visible or " print out " image. This would seem

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FRIESER—Microcinematographic Investigations on the Direct Blackening and Development of Silver Bromide Crystals. Phot. Ind. **35** (1937) 853.

GUNTZ—The Action of Light on Silver Chloride. Phot. J. **45** (1905) 131.

HARTUNG—Photochemical Decomposition of Silver Chloride. J. Chem. Soc. (London) **127** (1925) 2691.

HARTUNG—Photochemical Decomposition of Silver Iodide. J. Chem. Soc. (London) **129** (1926) 1349.

JONES AND BLAIR—The Effect of Concentration on the Production of the Latent Photographic Image by Hydrogen Peroxide. J. Chem. Physics **5** (1937) 835.

KEISER—Zeit. wiss. Phot. **26** (1928) 1.

KOCH AND VOGLER—Ann. d. Physik **77** (1925) 495.

STOCK—The Photochemical Decomposition of Silver Bromide. Zeit. wiss. Phot. **24** (1925) 132.

SCHWARZ AND GROSS—Z. anorg. Chem. **133** (1924) 389.

TRIVELLI AND SHEPPARD—Visible Decomposition of Silver Halide Grains by Light. J. Phys. Chem. **29** (1925) 1568.

to indicate that both involve basically the same reaction and that the visible image is the continuation of the same process which produces the latent image.

Reactions of the Latent Image.—Since the latent image cannot be subjected to direct chemical analysis, its reaction has been extensively studied and the results made the bases of numerous theories of latent image formation. The literature on this subject is enormous.[3] The following is an attempt to summarize briefly some of the more important reactions of the latent image from the standpoint of latent image theories.

1. *The latent image is weakened or destroyed by chemical oxidizing agents.* Substances such as potassium cyanide, potassium permanganate, ammonium sulfate, chromic acid and cupric, ferric and mercuric salts, when used with a halide, such as potassium bromide, weaken or destroy the latent image, depending upon the concentration, time of immersion, etc.

2. *Destruction of the latent image by oxidizing agents does not necessarily destroy sensitivity;* chromic acid, for example, was found to reduce the latent image to a much greater degree than the sensitivity, and with ammonium persulfate the difference is even greater.

3. *The latent image is not soluble in hypo, or other solvents of silver halide.* An image may be developed after fixing by the use of a solution of acid silver nitrate containing a reducing agent in which colloidal silver will be formed. This reducing agent must be a developer, however, as other reducing agents such as formaldehyde which will

[3] The most convenient reference for the student is Bullock, *Chemical Reactions of the Photographic Latent Image.* Van Nostrand 1927.

Sterry—The Action of Oxidizers on the Latent Image. Phot. J. **47** (1907) 170; Brit. J. Phot. **54** (1907) 166, 171, 206.

Sheppard and Mees—Action of Substances on the Latent Image. Phot. J. **47** (1907) 65; Brit. J. Phot. **54** (1907) 33.

Sheppard, Wightman and Trivelli—Action of Arsenite and Oxidizing Agents. J. Franklin Inst. **198** (1924) 507, 629.

Bullock—Oxidizing Agents and the Latent Image. Brit. J. Phot. **74** (1927) 590.

Clark—Oxidizing Agents in the Study of Sensitivity of Photographic Emulsions. Brit. J. Phot. **74** (1927) 227, 243.

Lumiere and Seyewetz—Development of the Latent Image after Fixation. Compt. rend. **178** (1924) 1765.

Owen—Physical Development and Nature of the Latent Image. Phot. J. **69** (1929) 278.

form collodial silver, under such conditions, will not develop the latent image.

4. *The latent image is produced, but at a slower rate, at the temperature of liquid air.*[4]

5. *The latent photographic image is destroyed by acids which dissolve silver,* e.g., nitric.

6. *The latent image may, under certain circumstances, develop as a positive instead of a negative image* (*photographic reversal*). Reversal is delayed by derivatives of hydrazine, phenylenediamine, sodium nitrite and certain other substances which absorb free halogen and is facilitated by sodium arsenite, hydrogen peroxide, potassium permanganate, persulfate and dichromate.

If an emulsion is given a preliminary exposure to white light and exposed a second time to light of a longer wave length (orange or red), the first image is partially destroyed (*Herschel effect*).

If an emulsion is greatly over-exposed and then treated with chromic acid, which destroys the latent image, and then exposed a second time and developed, a positive image is obtained (*Albert effect*).

If an emulsion is exposed briefly to a highly intense source of light, as for example a flash of lighting, and is then exposed to light of a much lower intensity, the first image is partially destroyed (*Clayden and Villard effects*).

Certain desensitizing dyes, such as phenosafranine, result in the reversal of the image following a preliminary flash exposure (*Luppo-Cramer effect*).

Historical Theories of the Latent Image.—Carl Wilhelm Scheele, who may in some respects be called the father of photo-chemistry, proved that chlorine is liberated when silver chloride darkens upon ex-

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[4] Bunsen and Roscoe, *Pogg Ann.* **108** (1876) 193; Dewar *Proc. Roy. Inst.* **13** p. 695.

Berg—Latent-Image Formation at Low Temperatures. Trans. Faraday Soc. **35** (1939) 445.

Carroll and Kretchman—Photographic Reversal by Desensitizing Dyes. Bur. Stand. J. Res. **10** (1933) 449.

Clark—Reversal by Hydrogen Peroxide, Sodium Arsenite and Light. Phot. J. **64** (1924) 363.

Stevens and Norrish—Border Effects Associated with Photographic Reversal Processes. Phot. J. **77** (1937) 314.

Stevens and Norrish—Mechanism of Photographic Reversal. Phot. J. **78** (1938) 513.

posure to light. According to Waterhouse,[5] Berthollet was the first to suggest that the latent developable image consisted of a sub-halide, i.e. silver halide containing less halogen than the normal. The sub-halide theory was stoutly defended by many of the most prominent authorities throughout the past century, and in some quarters well into the present, despite the failure of all attempts to prepare silver sub-halides in the laboratory.[6]

Arago in his paper on the Daguerreotype process, delivered to the Academy of Sciences (Paris) August 1839, expressed the opinion that the action of light resulted in the liberation of the halogen from the silver halide, so that some of the silver halide is reduced to metallic silver. Guthrie (1850), however, was apparently the first to develop the idea into a definite theory. He suggested that the action of light resulted in the liberation of halogen and the formation of small centers of metallic silver in the silver halide grain on which the image is built up in development by the deposition of silver from the developing solution. (It will be remembered that at that time acid developers containing silver were in general use.) So widely held, however, was the sub-halide theory that the metallic, or nascent silver theory, found only limited support.[7]

Renwick renewed interest in the metallic silver theory at a much later date [8] by suggesting that the effect of light is to coagulate amicrons of colloid silver which exist in an emulsion before exposure, and thus create centers of metallic silver which are of sufficient size to function as centers for the reduction of the grain to metallic silver by the developer. The colloid silver present in the emulsion is the result of the reduction of some of the silver halide in the digestion of the emulsion with heat or ammonia.

Throughout the last century when the sub-halide theory was more or less generally accepted, there were a few who maintained that the energy required to produce a latent image was insufficient to produce chemical change in the silver halide. Those who took that stand insisted that the light absorbed results in a physical rather than a chemical change in the silver halide. These so-called "physical theories" involve (1) the formation of an internal strain within the silver halide molecule which renders it unstable and therefore more readily reduced by the developer (*molecular strain theory*); (2) the breaking down of the silver halide into smaller particles which are more susceptible to reduction by the developer (*disintegration theory*); (3) the discharge of an electron, or electrons, leaving an unstable silver halide crystal (*photo-electric theory*).

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[5] Waterhouse, *Phot. J.* **47** (1903) 59.

[6] Vogel, *Phot. Mitt.* **36** p. 334; Von Bibra, *J. für Prak. Chim.* **2** p. 12.

[7] Mercator, *Brit. J. Phot.* **46** (1899) 628.

[8] Renwick, *Brit. J. Phot.* **67** (1920) 447, 463; **70** (1923) 382.

Investigations of the structure of the silver halide crystal during the last quarter of a century, largely by means of x-ray crystallography, led to the conclusion that no chemical molecule, in the sense of a specially combined atom pair, exists, but rather a space-lattice structure of silver ions and bromine ions, held together by the electrostatic attractions of the oppositely charged ions, and under such conditions there is little basis for physical theories which involve molecular strain or disintegration.

It has been established also that silver halides do not exhibit the true photo-electric effect at wave lengths greater than 280 millimicrons while, of course, the photographic response of silver halide without sensitizing extends to radiation of much longer wave lengths. There are many striking similarities, however, in photographic sensitivity and the *photo-conductivity* of silver halides, and theories of this type have not been abandoned but rather have developed beyond their original concept in accord with the developments in the fields of electronic theories of matter and energy,

The Primary Process in the Formation of the Latent Image.—The fact that upon continued exposure a silver halide is decomposed into silver and bromine suggests, although it does not definitely limit the developable or latent image to metallic silver, the latent and the visible image being thus regarded simply as two phases of a single reaction differing in degree but not in character. The chemical reactions of the developable image—summarized excellently by Bullock[9]—are not inconsistent with the view that it consists of metallic silver.

[9] Bullock, *Chemical Reactions of the Photographic Latent Image.* Van Nostrand (1927).

Allen—The Formation of the Image on the Photographic Plate. Phot. J. **54** (1914) 175. ....

Arens and Luft—Present Position of the Theories of the Latent Photographic Image. Veroffent. wiss. Zentral-Lab. phot. Abt. Agfa **4** (1935) 1.

Luppo-Cramer—History and Theory of the Latent Image. I. Zeit. wiss. Phot. **23** (1924) 91; II. Ibid. **23** (1925) 122; III. Ibid. **23** (1925) 216.

Renwick—The Gelatin Emulsion and the Latent Image. Brit. J. Phot. **70** (1923) 382.

Furthermore, no other explanation of the process of development so well fits the known facts as that based upon the existence of a deposit of metallic silver on the grain of silver halide to serve as a center for the reduction of the entire grain to metallic silver. If the view that the latent photographic image consists of silver is accepted [10]—and the evidence on this point is almost overwhelming—the problem becomes one of explaining how this silver is formed.

A molecule of silver halide, like all molecules, consists of atoms bound together by electrostatic forces. In the case of a molecule of silver bromide, the atoms of silver and bromide by sharing electrons—the binding force between atoms—are united to form a crystal lattice structure of the type shown in Fig. 205. These atoms are ionized since they are either accepting or giving up electrons, and, therefore, the silver atoms carry a positive charge, the bromine atoms a negative charge. Silver chloride and silver iodide, as well as silver bromide, crystallize in the simple cubic structure illustrated. Now, if the latent image is to be regarded as consisting of metallic silver, it is obvious that the action of light must be to cause one of the silver atoms (Ag+) to become an unionized atom. To accomplish this, it is necessary for it to receive an electron to neutralize its positive charge. This electron must come from the neighboring bromine ions; so that the action of light on the molecule of silver bromine is to cause the bromine ion to give up an electron which is accepted by a nearby silver ion to form a neutral atom of silver. The bromine ion, having given up its electron, is freed thus upsetting the balance of forces which existed in the molecule of silver halide.

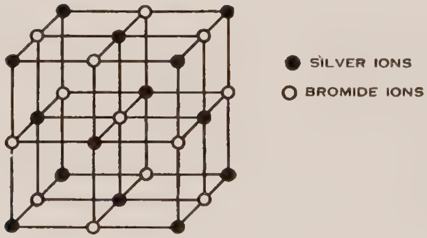

Fig. 205.

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[10] There are, however, some exceptions. For a recent theory of the latent image formation which does not regard the developable image as consisting of metallic silver, see Evans and Hanson, *Phot. J.* 77 (1937) 497.

This conception of the preliminary process in the formation of the latent photographic image, which is in full accord with modern theories of the mechanism of chemical processes, may be represented as follows:

$$\begin{aligned}&\mathrm{Br}^- + h\nu \rightarrow \mathrm{Br} + \text{electron}\\&\mathrm{Ag}^+ + \text{electron} \rightarrow \mathrm{Ag}\end{aligned}$$

It is clear that this reaction takes place not once but many times in a single grain, since for a grain to be made developable it would appear that this process must be repeated a sufficient number of times to produce a center of silver of sufficient size to provide a nucleus for development.

Role of the Sensitivity Centers.—It is reasonable to assume that light is absorbed over the entire exposed surface of the grain. Hodgson found, however, that development begins at certain discrete points on the grain from which it spreads out until the entire grain is reduced to metallic silver. This fact was confirmed later by the work of Svedberg and others and would seem to indicate that the silver atoms of the latent image are not spread uniformly over the grain but are concentrated at certain points. The work of Sheppard, Trivelli, Wightman, Loveland and others indicates that the silver atoms formed upon exposure to light are concentrated about the sensitivity centers or nuclei, which have been shown to consist of silver sulfide (Page 242). The silver sulfide specks, or sensitivity centers, promote sensitivity therefore, by concentrating the silver atoms formed during the exposure to light thus producing concentrations of silver at discrete points on the grain which are of sufficient size to render the grain developable.

There have been several attempts to explain the mechanism whereby light which is absorbed over the entire exposure area of the grain pro-

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Friedman—The Latent Image. Amer. Phot. (1940) 452.

Kornfeld—Distribution of the Latent Image of the AgBr grain. J. Opt. Soc. Amer. **31** (1941) 598.

Mees—Photography and Pure Science. J. Franklin Inst. **226** (1938) 281 (Theory of Latent Image).

Mott—A Description in Terms of Atomic Physics of the Action of Light on Photographic Emulsions. Phot. J. **78** (1938) 286.

Webb—The Photographic Latent Image Considered from the Standpoint of Quantum Mechanics. Phot. J. **77** (1937) 142.

Webb—Theory of the Photographic Latent Image Formation. J. Applied Phys. **11** (1940) 18.

Webb—The Formation of the Photographic Latent Image. J. Phot. Soc. Amer. **7** (1941) 136.

duces silver atoms only about the sensitivity centers or sulfide specks. Sheppard, Trivelli and Loveland proposed what is commonly termed the *Concentration-Speck* Theory (1925). This theory assumes that the energy absorbed throughout the grain is transferred by radiationless collisions until the sensitivity center is reached. Thus energy absorbed at one point on the grain is absorbed by the electron of a Br^- ion and its energy raised, this energy being then transferred from one atom to another until the sensitivity center is reached at which point the Br^- ion is released and a silver atom formed. While this assumption is not entirely satisfactory, the basic idea of the function of the sensitivity center in concentrating the silver formed on exposure is generally accepted.

In 1928 Trivelli suggested[11] that in view of the photoconductivity properties of silver bromide and the photo-voltaic effect at Ag: AgBr electrodes, the mechanism of the formation of the latent image is similar to the action within an electrolytic cell.

The silver sulfide sensitivity center is assumed to act as an anode and the silver as the cathode, while the solid silver bromine is the electrolyte. On exposure to light electrons pass from the silver sulfide through the silver bromide to the silver, while the silver cations of the silver bromide are attracted to the silver cathode. Thus the silver originally present increases in size by the electrolytic disposition of silver until it reached the developable size. While this theory has certain attractive features, it has not been possible to prove that such a reaction will take place in a similar large-size cell and hence it has not met with widespread acceptance.

In 1938 Gurney and Mott proposed an extension of the concentration speck theory which has received considerable attention.[12]

The extension is in providing a more detailed explanation of the way in which the energy absorbed at various points on the grain is concentrated to form silver only about the sensitivity centers. The explanation is based upon the photoconductivity and electrolytic conductivity of silver bromide. Measurements of the photo-conductivity of silver bromide have indicated that for each quantum of light absorbed by a silver bromide grain, an electron is released and that this electron can move about freely in the crystal. These electrons are trapped, or held, by the centers of silver sulfide forming the sensitivity centers.

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[11] *J. Franklin Inst.* **204** (1927) 649; **205** 111. *Nature,* **120** (1927) 728.

[12] Gurney and Mott, *Proc. Royal Soc.* **164A** (1938) 151. Mott, *Phot. J.* **78** (1938) 268. Berg, *Nature* **140** (1937) 997.

The electrons so held charge the speck of silver or silver sulfide negatively. This negative charge thereupon sets up an electrostatic field within the grain so that positive charges are attracted. Thus Ag^+ ions in the lattice are attracted to the silver centers where they neutralize the electrons there to form silver atoms. Thus, the speck grows by a repetition of the process; one atom of silver being produced by each quantum absorbed.

This theory is in full agreement with the condition of quantum equivalence, since one atom of silver is formed for each quantum of light absorbed. It also provides an explanation of the mechanism whereby light, which is absorbed over the entire exposure area of the grain, can produce silver atoms only at certain points which is in accordance with the photo-conductance of silver bromide. It is founded on well-accepted conceptions of atomic physics and, in addition, it is successful in explaining some of the properties of the latent photographic image, such as reciprocity law failure, the Herschel effect, the intermittency effect, and others, which do not fit in so well with other theories.

PART II

THEORY OF DEVELOPMENT

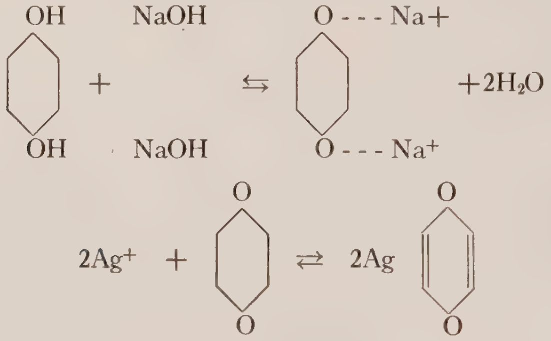
The operation by which the invisible, or latent, photographic image is made visible is known as development. Since the exposure required to produce a visible image is many times that required to produce an image which may be made visible by development, the latter is in effect a means of multiplying the result produced by light so that an almost infinitesimal exposure of the sensitive silver halide grain may be converted into a substantial image.

If the latent photographic image is regarded as consisting of minute nuclei, or centers, of silver on the grains of silver halide affected by light, development consists essentially in the formation of sufficient additional silver about these nuclei to produce a visible image. The added silver required to produce a visible image may be the result (1) of preferential deposition of silver from a silver-containing solution (the so-called "physical" development), (2) or the reduction of the grains of silver halide containing a nucleus (i.e., exposed grains) to silver ("chemical" development). While it is possible that negative development involves both types to a limited extent, only the latter phase will be discussed here.

Development as a Process of Chemical Reduction.—Chemical development is thus a process of chemical reduction and consists in the conversion of ionic to metallic silver; in other words, there is an exchange of electrons between the ionized silver halide and the developing agent. The silver cation receives an anion from the developer which removes its positive charge, and it becomes metallic silver. The bromine anion is fixed in the form of an organic, or metallic, bromide depending upon the nature of the developing agents. Owing to the complex constitution of the organic developing agents, it is difficult to be more precise on this point. With ferrous oxalate, the reaction is

$$Fe_2C_2O_4 + K_2C_2O_4 \rightarrow K_2Fe_2(C_2O_4)_2$$
$$6K_2Fe(C_2O_4)_2 + 6AgBr \rightarrow 2FeBr_3 + 6Ag + 2Fe_2(C_2O_4)_3 + 6K_2C_2O_4$$

Among the common organic developers, alkaline hydroquinone, used without sulfite, is the only one which has been studied in detail. According to Sheppard, the reaction is as follows:



Theories of Development.—Microscopic studies of development by Sheppard and Mees,[13] Hodgson,[14] and Svedberg[15] reveal that development starts at discrete points on the surface of the silver halide grain and proceeds until the entire grain is reduced to metallic silver. Observations by Hilsch and Pohl have shown specific adsorption of photosilver centers in silver halides. Recent work with the electron microscope[16] at Kodak Research Laboratories show that fine filaments or thread-like protuberances are formed when the grain is developed.

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[13] Sheppard and Mees, *Investigations of the Theory of the Photographic Process*, Longmans (1907).

[14] Hodgson, *Brit. J. Phot.* **64** (1917) 654.

[15] Svedberg, *Phot. J.* **61** (1921) 325; **62** (1922) 186.

[16] Mees, *J. Soc. Mot. Pict. Eng.* **37** (July 1941) 15.

Theories of development are quite involved and complex. In general, these may be grouped under two heads as: supersaturation and adsorption theories. But since parts of some theories overlap parts of another, while others incorporate ideas common to both, no attempt will be made to assign theories to either group. The theories will, therefore, be discussed in chronological order.

The oldest accepted theory of development is that proposed by Ostwald, which assumes that the silver produced by the reduction of silver bromide is deposited on specks, or nuclei, of the grain. Abegg and Schaum modified and elaborated on this theory, accordingly;—as the silver halide dissolves in the developing solution, the silver ions are reduced to metallic silver and the solution becomes rapidly supersaturated with respect to silver. The process then continues until the reaction comes to equilibrium and reduction of silver ions ceases. However, if silver nuclei of the latent image are present, silver from the solution deposits on the nuclei. This upsets the equilibrium and causes further reduction to take place.

Bancroft [17] proposed the first adsorption theory in 1913. His theory is based on the assumption that if the reducing agent is adsorbed more strongly to the exposed silver halide than to the unexposed, the former will develop more rapidly because of the greater concentration at the surface of the exposed silver halide grains.

Sheppard in 1919 [18] suggested that an important phase of development consists in the formation of a complex between silver bromide and the reducer, which undergoes internal rearrangement and decomposition into metallic silver, which is more or less colloidal, and is adsorbed to the residual silver halide.

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[17] Bancroft, *Trans. Farad. Soc.* **19** (1923) 251.

[18] Sheppard, *Phot. J.* **59** (1919) 136.

De Langhe—Theory of Photographic Developability. Z. wiss. Phot. **35** (1936) 201.

Evans and Hanson—Photographic Development and the Latent Image. Phot. J. **77** (1937) 497.

Homolka—The Latent Image and Development. Brit. J. Phot. **64** (1917) 81.

Matthews and Barmeier—The Electro-potentials of Certain Photographic Developers and a Possible Explanation of Photographic Development. Brit. J. Phot. **59** (1912) 879.

Later, in 1920, Sheppard and Mayer pointed out the importance of the silver halide interface.[19] They assumed that the developer is adsorbed to the solid silver halide forming a complex between silver ions and the developing agent which in the presence of the latent image becomes reduced to metallic silver and an oxidized developer.

Volmer, 1921, supposed that the silver of the latent image catalysed the reaction between silver bromide and the developer. Because colloidal silver increased the rate of aerial oxidation of the developer, he concluded that it would catalyse the reduction of silver halide.[20]

Schwartz, 1933, proposed a theory that neglects the presence of nuclei. On the basis of experiments he concluded that collodial silver bromide solutions are not reduced, but that coagulation of the sol is necessary for the first stage of development.[21] Exposure to light removes the negative charge from the surface of the colloidal particle, and allows the negative ion of the developer to react. Fogging without exposure is due to the absence of electrostatic repulsion between positive charged emulsion particles and the developer ion.

Reinders, 1934, restated the Ostwald theory.[22] He pointed out that an equilibrium is set up and that under suitable conditions the reverse reaction would predominate. He determined the concentration of silver by the oxidation-reduction potential of the solution. Reinders applied the Ostwald solubility law to silver particles of the latent image. This law states that small particles are more soluble than large ones. According to the theory, if a solution having a concentration of metallic silver, C, is just saturated with respect to particles of size A, then for particles larger than A it will be supersaturated, and these will act as nuclei for crystallization. Particles which are smaller than A will dissolve. A developer to develop particles of size A must have a

[19] Sheppard and Mayer, *J. Am. Chem. Soc.* **42** (1920) 689.

[20] Volmer, *Z. wiss. Phot.* **20** (1921) 189.

[21] Schwartz, *Phot. Korr.* **31** (1933) 265.

[22] Reinders, *J. Phys. Chem.* **38** (1934) 783.

MURRAY—A Theory of Photographic Development. Phot. J. **77** (1937) 388.

PANDALAI—Mechanism of Photographic Development. J.S.C.I. **54** (1935) 169T.

RABINOVICH—The Mechanism of Development. J. Phys. **5** (1934) 232. Sci. et Ind. Phot. (II) **5** (1934) 250.

RABINOVICH—Theories of Photographic Development. Proc. Ninth Int. Congress of Phot. Paris, 1935. Sci. et Ind. Phot. (II) **6** (1935) 295.

reduction potential low enough to reduce silver bromide and produce a silver concentration higher than C. Since the potential for the solution of smaller particles will be lower than that corresponding to the solubility of the large particles, a stronger reducing agent is required for the development of the smaller particles.

Rabinovitch, 1934, postulated an adsorption theory, in which the developer was adsorbed to the silver of the latent image but not to silver bromide.[23] A high concentration of developer in neighborhood of the nuclei caused adjacent silver bromide to be reduced. Following reduction, more developer is adsorbed to silver and the process is repeated.

Murray in 1937 introduced a theory of development which emphasized the importance of the induction period.[24] The process which takes place during the induction period is assumed to determine whether an exposed grain will develop or not. The main assumptions of this theory are: The reduction of the silver halide grain of the emulsion by developing solutions takes place at points on the grain surface where silver ions of the crystal lattice are not covered by adsorbed ions. The reduction is catalysed at the interface between reduced metallic silver and silver halide. The effect of light on the silver halide grain produces a silver deposit in the neighborhood of development centers which is permeable to substances in solution.

Evans and Hanson presented in 1937 an adsorption potential theory of development.[25] Development is assumed to be of two types: Chemical and Chemical-Physical. As summarized by the authors, chemical development consists of three simultaneous steps: "(1) The developing agent, governed by its molecular structure and the ionic nature of the solution, is adsorbed to the silver halide crystals, a characteristic equilibrium being set up for each crystal; (2) The developing agent so

[23] Rabinovitch, *Z. wiss. Phot.* **33** (1934) 57.
[24] Murray, *Phot. J.* **77** (1937) 388.
[25] Evans and Hanson, *Phot. J.* **77** (1937) 497.

Sheppard—The Electro-chemistry of Development. Trans. Electrochem. Soc. (1921) 429.

Sheppard and Elliott—On the Theory of Development. Trans. Faraday Soc. **19** (1923) 355.

Sheppard and Mees—Some Points in Modern Chemical Theory and their Bearing on Development. Phot. J. **45** (1915) 241.

Volmer—The Theory of Development of the Latent Photographic Image. Z. wiss. Phot. **20** (1921) 189; Phot. Korr. (1921) 226.

adsorbed attains a definite reduction potential due to its activation by the solution; (3) If the potential so set up is greater than the surface potential of the crystal at any point, electrons are sent into the crystal lattice and the crystal is converted to metallic silver, bromide ions being released into the solution. The last step may be autocatalytic, since each electron which enters the lattice can decrease the work function of the surface." Chemical-physical development "is due to the solvent action of the developer on the silver halide of the emulsion, silver complexes being formed and immediately reduced by the developer to metallic silver, giving rise to a supersaturated solution. This solution is deposited on any nuclei present, such as those due to solarization of electron concentrations or to chemically developed grains. The velocity of chemical-physical development is set by the rate of solution of the halide, and so may be very fast as compared to the customary post-fixation physical development." The theory is shown to include present accepted theories and is able to account for the effects of solarization, densensitization, action of oxidizing agents, and "elimination" of solarization by bromine acceptors.

Staude has discussed the role of oxidation products in processes of development [26] and James [27] has studied the surface conditions of silver halides and the rate of reaction. Measurements of the reduction of silver chloride by various reagents were made.

[26] Staude, *Z. wiss. Phot.* **38** (1939) 65–96.

[27] James, *J. Am. Chem. Soc.* **62** (1940) 1654–1658.

ARMSTRONG AND WEISSBERGER—Effect of Resonance on the Activity of Some Developing Agents. J. Amer. Chem. Soc. **63** (1941) 182.

DAVEY—The Theory of Development. Phot. J. **75** (1935) 433.

EVANS AND HANSON—Photographic Development and the Latent Image. Phot. J. **77** (1937) 497.

JAMES—Mechanism of Development. J. Phys. Chem. **43** (1939) 701.

JAMES—Mechanism of Photographic Development. Development by Hydroquinone. J. Phys. Chem. **44** (1940) 42.

JAMES—Mechanism of Photographic Development. III. Developing and Non-Developing Reducing Agents. J. Amer. Chem. Soc. **62** (1940) 3411.

JAMES—Some Experimental Basis for the Development Process. Phot. Tech. **2** (1940) 54; **3** (1941) 49.

RABINOVITCH—Absorption Theory of Development. Trans. Faraday Soc. **34** (1938) 920, 936.

REINDORP—The Theory of Development. Brit. J. Phot. **84** (1937) 669.

Color Development.—A number of organic components which act as developing agents produce images that consist of a dye as well as the usual silver image. The developing agent, in this case, may be regarded as a dye intermediate which functions as a developer, producing a silver image and is itself transformed in the reduction of the silver halide to form a dye image. Among the best known developing agents of this type are pyrogallol,[28] pyrocatechin, indoxyl, thioindoxyl, 4-methoxy-alphanaphthol, and hydroxy-coerulignon. Of these the best known are indoxyl and thioindoxyl, which were studied in some detail by Homolka.[29] This method of producing color dye images is termed *primary color development.* In practice such methods have not been successful because (1) the images are relatively unstable, (2) the highlights are frequently stained, and (3) the range of colors obtainable is limited.

In 1912 Fischer[30] found that silver and dye images may be obtained by adding suitable amines, or phenols, to certain developers such as, para-aminophenol and paraphenylene diamine. The dye image in this case is formed by the coupling (condensation) of the oxidized developing agent and the amine or phenol. The term "color development" was applied to the process by Fischer and his co-worker Siegrist,[31] and the term "coupler" to the second component. This method of producing dye images by development is termed *secondary color development.*

Fischer also patented[32] the use of such processes for the production of prints in color and for color photography. His patent included images consisting of dyes belonging to five different classes, namely: indophenols, indoanalines, indiamines, indothiophenols, azomethines, to which may be added a sixth class including leuco derivatives of these dyes, as follows:

1. Indophenols—formed during development, with a para-aminophenol and a phenol.

$$H_2N.C_6H_4.NH_2 + C_6H_5OH \xrightarrow{O_2} HO.C_6H_4N{=}C_6H_4{=}O + 2H_2O$$

2. Indoanalines—formed with a paraphenylenediamine and a phenol.

$$H_2N.C_6H_4.NH_2 + C_6H_5OH \xrightarrow{O_2} H_2N.C_6H_4.N{=}C_6H_4{=}O + 2H_2O$$

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[28] Liesegang, *Phot. Arch.* **36** (1895) 115.

[29] Homolka, *Phot. Korr.* **44** (1907) 55, 115; **51** (1914) 256, 471. *Brit. J. Phot.* **54** (1907) 136, 196, 216. Ermen, *Brit. J. Phot.* **70** (1923) 47, 299.

[30] Fischer, *Brit. J. Phot.* **60** (1913) 595, 712; **61** (1914) 329.

[31] *Phot. Korr.* **51** (1914) 18.

[32] U.S.P. 1,055,155; 1,079,757; 1,162,028. D.R.P. 253,335.

3. Indamines—formed with a paraphenylenediamine and an amine.

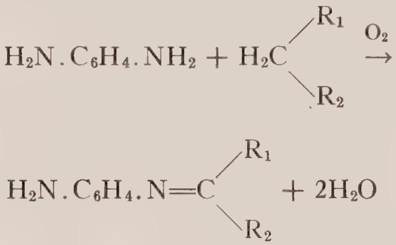
$$H_2N.CH.NH + C_6H_5.NH_2 \xrightarrow{O_2} H_2N.C_6H_4.N{=}C_6H_4{=}NH + 2H_2O$$

4. Indothiophenols—formed with a paraphenylenediamine and a thiophenol.

$$H_2N.C_6H_4.NH_2 + C_6H_5SH \xrightarrow{O_2} HS.C_6H_4.N{=}C_6H_4{=}NH + H_2O$$

5. Azomethines—formed with

$$\left.\begin{array}{c}\text{para-aminophenols}\\ \text{or}\\ \text{paraphenylenediamines}\end{array}\right\}\text{ and }\left\{\begin{array}{c}\text{compounds containing active}\\ \text{methylene groups.}\end{array}\right.$$



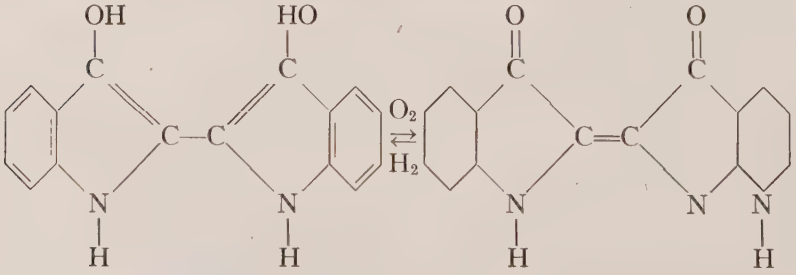
$$H_2N.C_6H_4.NH_2 + H_2C\begin{matrix}\diagup R_1\\ \\ \diagdown R_2\end{matrix} \xrightarrow{O_2}$$

$$H_2N.C_6H_4.N{=}C\begin{matrix}\diagup R_1\\ \\ \diagdown R_2\end{matrix} + 2H_2O$$

Typical couplers containing acid methylene groups are:

$CH_3COCH_2COOC_2H_5$	Aceto-acetic-ester
$C_6H_5COCH_2COC_6H_5$	Di-benzoyl-methane
$NO_2.C_6H_4CH_2CN$	Para-nitro-benzyl-cyanide

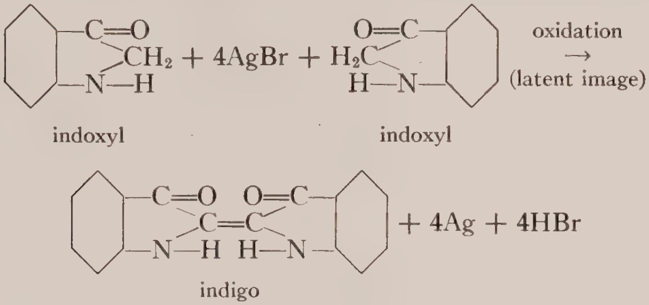
6. In addition to the above, a sixth class may include leuco derivatives of indigo, indophenols, indamines, azomethines or substituted quinones which act as developing agents and undergo oxidation forming colored substances that are substantive to gelatin.



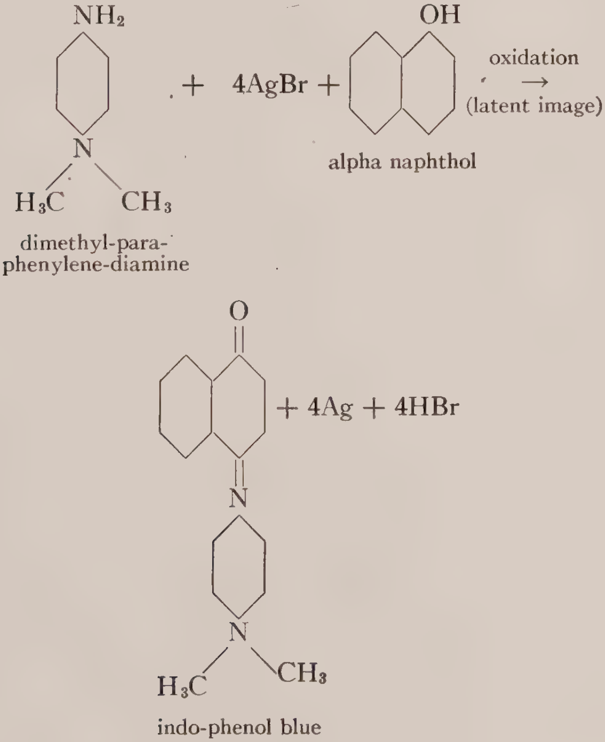
indigo, white (soluble) leuco base

indigo blue (insoluble) dye

The Chemistry of Color Development.—The reaction with indoxyl may be taken as characteristic of primary development.

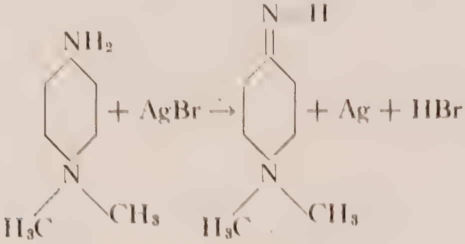


The reaction between dimethyl-paraphenylene-diamine (developing agent) and alpha naphthol (coupler) serves to illustrate secondary color development.



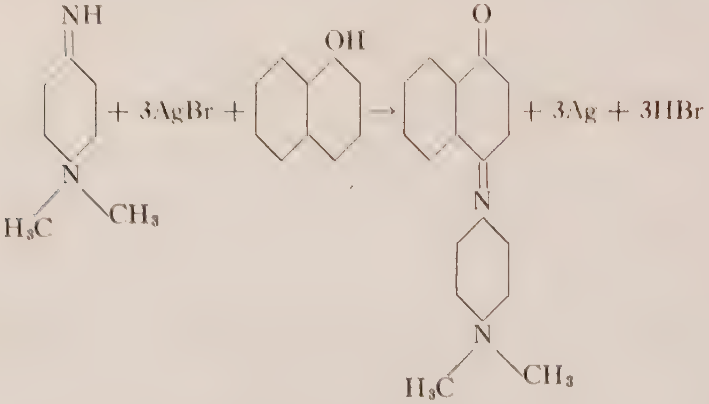
Tull[33] has shown that the dye coupling reaction may also take place in two steps.

Step 1. The diamine is oxidized to monoquinoneimide:



(diamine) (imide)

Step 2. The oxidized developing agent is coupled to a coupler.



In either case, 4 atoms of silver are developed for every molecule of dye that is formed. This fact is also confirmed in an Agfa patent.[34]

Production of Dye Images by Coupling with Dyes.—While in preceding sections color development has been discussed in connection with the latent image only, the same result may be produced by other images. In photography, as in the dye industry, the formation of dyes by coupling is accomplished by means of oxidation. The dye industry employs oxidizing agents while images may accomplish the same purpose in photography. In various photographic processes, chromate images, silver images, latent images and silver-dye images have been used as a means of oxidation. Besides serving as an oxidizing medium, the silver or chromate image also serves to control the position of the dye image formed in the emulsion. For convenience of discussion, the development of dye coupling may be divided into four sections according to the type of image employed:

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[33] Tull, *Brit. J. Phot.* **85** (1938) 627.

[34] Agfa, B.P. 464,398.

1. *Chromate Images.* The use of chromates for the production of colored images is the oldest of the dye-coupling processes and dates back to work of Hannaford [35] in 1860. Other workers employing chromate images were Willis, Kopp, Guserson and Andresen, Vidal and Thiebault.

Dye coupling by means of chromate images has been accomplished in the following ways:

a. An albumen emulsion containing dichromate, ferric ammonium citrate and gallic acid.
b. Fuming acidified dichromate images with aniline vapors.[36]
c. The use of chromate images for the oxidation of organic compounds that form insoluble colors.[37]
d. Addition of developing agents to washed dichromate emulsions.[38]
e. Treating chromate images with certain amines and phenols.[39]
f. Addition of dichromate to a paraphenylenediamine mixture.[40]

2. *Silver Images.* Silver images acting as catalysts for subsequent reactions, or salts resulting from silver images, may furnish the necessary oxidation for dye coupling.

Silver images are usually transformed into salts as chlorides, bromides and ferrocyanides which are capable of reacting with aniline derivatives and forming dyes.[41]

3. *Latent Images.* Latent images may also serve as oxidizing agents.

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[35] Hannaford, *Brit. J. Phot.* **7** (1860) 100.

[36] Willis, Brit. P. 2800 (1864).

[37] Kopp, *Chem. News* (London) **9** (1884) 296; **10**, 28.

[38] Guserson and Andresen, D.R.P. 116,177 (1900); Brit. P. 12,313 (1900).

[39] Brit. P. 5879 (1901). Thiebault, *Brit. J. Phot.* **55** (1908) 738.

[40] Vidal, F.P. 391,465.

[41] Richard, *Compt. rend.* **122** (1896) 609. Fischer, Brit. Pat. 5602 (1913); U.S.P. 1,079,756.

The staining of silver images developed with agents like pyrogallol and amidol was observed by Liesegang.[42] The stain was due to the formation of insoluble dyes [43] which resulted from the oxidation of the developing agents and was found to be proportional to the silver density.[44] The use of a sufficient amount of sodium sulfite was found to prevent stain. However, when a color image is desired, it is necessary to use developers which produce a stain or color.

With the use of developing agents, which are dye intermediates, color images may be formed by either primary or secondary development, as previously discussed. It will be recalled that certain dye intermediates act as developing agents and produce color.[45] Others require the addition of couplers for color formation.[46] Couplers may be incorporated in the emulsion or added during processing.[47] If couplers are incorporated in emulsions, it is necessary to prevent diffusion during coating and development. This is accomplished: by employing reagents containing one or more groups having substantive properties [48]; by the use of compounds having high molecular weight [49]; or by the addition of precipitants.[50]

Removal of the silver image with solutions, like Farmer's reducer, leaves the insoluble dye image in the emulsion.

[42] Liesegang, *Phot. Arch.* **36** (1895) 115.

[43] Lüppo-Cramer, *Phot. Korr.* **42** (1905) 319; **43** (1906) 242.

[44] Watkins, *Phot. J.* **36** (1896) 245.

[45] Homolka, *Phot. Korr.* **44** (1907) 55, 115; Eders Handbuch, Vol. **4** Pt. 2, p. 525.

[46] Fischer, *Chem. Zeitung* (1912) 696; *Phot. Korr.* **51** (1914) 18.

[47] Fischer, U.S.P. 1,102,028.

[48] Agfa, F.P. 844,637. D.R.P. 503,732.

[49] Eggert, D.R.P. 52,094 IV 6, 576.

[50] Kodak, A.G.-D.R.P. 631,324.

WALL—History of Three Color Photography.

FRIEDMAN—Color Development. Amer. Phot. **34** (1940) 914; **35** (1941) 62.

FISCHER AND SIEGRIST—The Formation of Dyestuffs by Oxidation by Means of Exposed Silver Halide. Phot. Korr. **51** (1941) 18.

The Photographic Chemistry of the New Color Film Processes. Die Photographische Industrie **34**, 46/47, Nov. 11/18 (1936). Also Brit. J. Phot. **84** (1937) 67, 86.

THORPE AND LINSTEAD—Synthetic Dyestuffs and Intermediate Products. C. Griffin & Co., London. Revised Edition (1933).

4. *Silver-dye Images.* Dye images resulting from oxidation, or reduction, of dyes in contact with the silver image (Silver-dye Destruction process) may act as bases for coupling, or as generators for new dye images. This procedure has been employed in some of the Gaspar methods. See Chapter 33.

Color Processes Using Dye Coupling.—Most of the recent tripack color films and papers employ dye coupling development in the formation of the color images. The coupler components may either be incorporated in the emulsion layers or be present in the developing solutions. (See Chapter 33.)

For more recent advances dealing with development of chromogenic developers, new couplers, control of diffusion, and sensitivity of materials, the student is referred to the literature, particularly the abstract journals and patents. Excellent reviews are found in the sections on *"Progress in Color"* in the *British Journal of Photography* and in *"Color Photography"* and *"Photographic Reviews"* by Friedman in *American Photography.*

The Rate of Reduction.—There are three phases in the process of development to form a silver image: (1) the induction phase, (2) the reduction phase, (3) the precipitation phase.

Beginning with the surface of the emulsion layer, the developer rapidly diffuses through the gelatin and then more slowly penetrates the crystal of silver halide. This is followed by the progressive reduction of silver halide to silver, and the addition of silver thus formed to the original nucleus a process, which, assuming a constant supply of fresh developer, continues until the crystal is completely developed.

Diffusion plays a very important part in these reactions, and other things being equal, those crystals lying nearest to the surface of the emulsion layer will be penetrated and attacked first. Since the strength of the developer is being continually reduced by use, the development of the lower strata of silver halide grains will be delayed until the concentration of fresh developer is sufficient to initiate and complete the reduction of the silver halide. Consequently, in the development of negative emulsions, or emulsions of any considerable thickness, it is probable that all three phases of the developing process are taking place at the same time.

The time elapsing between the application of the developer and the first appearance of the image is known as the induction period and corresponds with the arithmetical coefficient of development. The induction period, with any particular developer, is a constant fraction of the time required for a given degree of development, but this arithmetical relationship is altered by soluble bromides and iodides, the former lengthening and the latter shortening the induction period.[51]

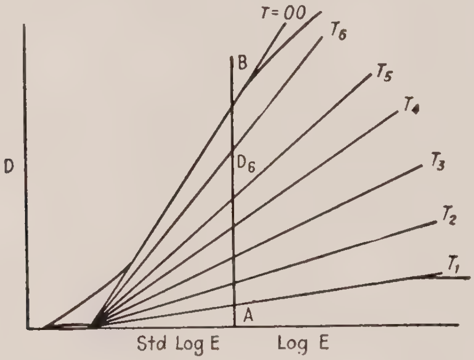

FIG. 206. Method of Determining the Increase in Density for a Given Exposure with Increased Development.

If, for a given exposure, the variation in density with the time of development is found by erecting a perpendicular from a point on the log exposure axis, so as to intersect the straight-line portions of a family of H and D curves (Fig. 206) and density is plotted as a function of the time of development, a curve of the exponential type (Fig. 207) is obtained. This indicates that the growth of density is rapid at first, becoming slower and slower as development proceeds until the latent image is completely developed when it ceases, except for the increase due to the development of unexposed silver halide (fog). The maximum density obtainable (*D* Max) depends chiefly upon the emulsion, but varies to some extent with different developers.

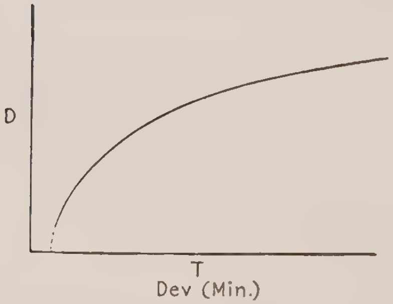

FIG. 207. Curve Representing the Relationship of Density and the Time of Development.

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[51] Sheppard, *Phot. J.* **45** (1905) 281; Sheppard, *J. Chem. Soc.* (London) **87** (1905) 1311; Sheppard and Meyer, *Phot. J.* **60** (1920) 12.

The explanation of this progressive diminution in the velocity at which density increases is quite simple, although it is a difficult matter to find a mathematical expression which will cover all conditions.

After development for any length of time short of that required to produce the maximum density, three kinds of grains are present:

A. Developed grains.
B. Developable but undeveloped grains.
C. Undevelopable grains.

The *A* grains represent the density already attained; the *A* and *B* grains together, the maximum density which can be secured exclusive of fog. The *B* grains, therefore, are the only ones subject to development and as the reaction proceeds the number of *B* grains will become less and less until finally when all are developed the process must stop. Thus the density undeveloped at any time t will be $(D_\infty - D)$, where D is the density developed at any time t and D_∞ the maximum density. Supposing that the rate at which the developer reduces the exposed, but undeveloped, grains is a constant and independent of the number of grains (as is actually the case) and that the rate of diffusion remains unaltered, we can express the rate of development, or dD/dt, as

$$\frac{dD}{dt} = k(D_\infty - D),$$

where k is a constant determined by the rate at which the exposed grains are reduced by the developing agent. This formula fits the case fairly well with acid developers over a moderate range but wide variations are observed with most alkaline developers and other more complex equations have been suggested to account for the various factors involved.[52]

[52] A comprehensive review of later work on the velocity of development and development velocity equations will be found in *The Theory of Development*, by A. H. Nietz.

Davidson—Conditions Governing the Behaviour of Silver Bromide Grain During Development. II. Phot. J. **66** (1926) 230–242.
Krohn—The Mechanism of Development of the Image in a Dry Plate Negative. Phot. J. **58** (1918) 179; Brit. J. Phot. **65** (1918) 412.
Luppo-Cramer—Topographical Relations in Development. Z. wiss. Phot. **24** (1926) 1–12.
Nietz—Theory of Development. Phot. J. **60** (1920) 280.

The constant k is termed the *velocity constant* of development. With any particular emulsion and developer, at a particular temperature, the value of k is a direct indication of the rate of development.

To determine the value of the velocity constant, k, the values of gamma for two sensitometric strips simultaneously exposed and developed for different times, of which one is double the other must be known. The values of γ^1 and γ^2 having been found, k may be calculated from the following equation:

$$k = \frac{I}{t_1} \log e \frac{1}{\gamma^2 - \gamma^1} \quad \text{or} \quad \frac{I}{t} \log_e \frac{D_\infty}{D_\infty - D},$$

where D_∞ = maximum density, D density at time t.

CHAPTER X

DEVELOPING AGENTS AND SOLUTIONS

Inorganic Developers.—The number of inorganic reducing substances which function as photographic developers is relatively small. The principal are:

Ferrous oxalate ($FeCl_2O_4$),
Ferrous fluoride ($FeFl_2$),
Sodium hydrosulfite ($Na_2S_2O_4$),
Hydrogen peroxide (H_2O_2),
Hydroxylamine (NH_2OH),
Hydrazine (N_2H_4),
Copper chloride ($CuCl$).

Most of these are of theoretical interest only. Ferrous fluoride, for example, functions as a developer in acid solution but is impractical because of the formation of hydrofluoric acid. Hydroxylamine forms a fairly vigorous developer in a strongly alkaline solution but nitrogen is produced and the emulsion layer disrupted. Ferrous oxalate and sodium hydrosulfite, however, while not in general use, are more worthy of attention since both form developers of practical utility. Ferrous oxalate, in fact, was for many years in general use as a negative developer, while sodium hydrosulfite has lately received some consideration as a developer for bromide prints for the carbro process.[1]

Ferrous oxalate functions as a developer only in the presence of an excess of potassium oxalate. This forms the double salt $K_2Fe\ (C_2O_4)_2$ which dissociates into

$$K_2Fe_2(C_2O_4)_2 \rightleftarrows FeC_2O_4 + K_2C_2O_4,$$

the actual developing ion being $Fe(C_2O_4)_2''$. Thus the reaction taking place in development may be represented [2] as

$$(C_2O_4)'' + Fe(C_2O_4)_2'' + Ag \rightleftharpoons Fe(C_2O_4)_3''' + Ag.$$

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[1] Durham, *Brit. J. Phot.* **87** (1940) 169; Brooks & Blair, *Phot. Tech.* **2** (1941), May, p. 12.

[2] Sheppard, *Photography as a Scientific Implement,* Van Nostrand (1923) p. 143.

As a developer ferrous oxalate is noteworthy for its fog-free, pure black, silver deposit. It does not, however, fully develop the latent image and greater exposure is necessary than with the more energetic organic developers. This is of no concern in the case of papers and transparencies for which it is well adapted on account of its freedom from stain and fog and the clean, neutral-black image.

For those who may wish to experiment, the following formula is suggested:

A.	Ferrous sulfate	330 gm.	5¼ oz.
	Water to make	1000 cc.	16 oz.
	Sulfuric acid	1 cc.	7 minims

Only the highest grade *ferrous* sulfate should be used and this should be fresh. This stock solution will keep for only one or two days.

B.	Potassium oxalate	330 gm.	5¼ oz.
	Hot water to make	1000 cc.	16 oz.

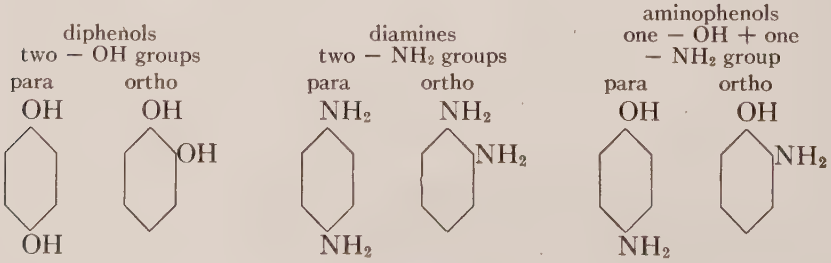
For use, take one part of *A* to four of *B*. Add *A* to *B*.

The following formula for sodium hydrosulfite has been recommended by Seyewetz as forming a rapid developer producing images of good contrast and comparatively free from fog, particularly with lantern slides and bromide papers:

Sodium hydrosulfite (80%)	100 gm.	1 oz.
Sodium bisulfite (60%)	165 gm.	1 oz. 285 gr.
Potassium bromide	35 gm.	154 gr.

For negative development 1 ounce 87.5 gr. (120 grams) of this mixture are dissolved in 10 ounces (1 liter) of water, while for most bromide papers and lantern slide plates twice this quantity of water should be used.

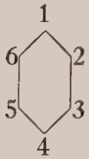
Organic Developers.—The organic developing agents in common use are all para or ortho diphenols, diamines or aminophenols as follows:



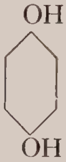
While there is some evidence to show that developing properties do not depend on the constitution of the reducing agent but simply on its reduction potential[3] the work of A. and L. Lumière, Seyewetz and Andresen has established certain general rules which apply to the organic developing agents known.

Compounds containing two hydroxyl (OH); two amino (NH_2) or one hydroxyl and one amino group.

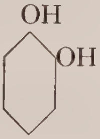
1. These substances are developers only if the groups occupy the 1 and 4 (*para*) or the 1 and 2 (*ortho*) positions in the benzene nucleus. For example:



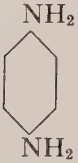
benzene



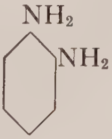
parahydroxybenzene
(hydroquinone)



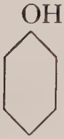
orthohydroxybenzene
(pyrocatechin)



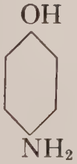
paraminobenzene



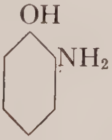
orthoaminobenzene



phenol



paraminophenol



orthoaminophenol

2. Substances in which the two substituted groups occupy the 1 and 4

[3] Maurer and Zapf, *Phot. Ind.* **33** (1935) 90; Abribat, *Phot. J.* **75** (1935) 434.

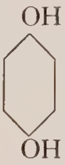
ANDRESEN—Organische Entwicklersubstanzen. Eder's Jahrbuch **7** (1903) 486.

LUMIÈRE AND SEYEWETZ—Developing Properties of *m*-Derivatives. Sci. et Ind. Phot. **8** (1928) 37.

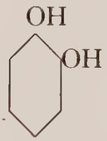
SEYEWETZ—The State of our Knowledge of Organic Developing Agents. Bull. Soc. franç. Phot. (1920) 129; Brit. J. Phot. **66** (1920) 186.

SEYEWETZ AND SZYMSON—Products of Oxidation of Photographic Developers by Silver Bromide. II. Bull. Soc. chim. 1 (1934) 1506.

or para position are more energetic developers than ortho (1:2) compounds. For example:

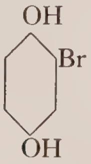


is more powerful than



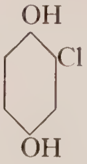
3. The dioxybenzenes are more energetic developers than the aminophenols, and these in turn are more energetic than the diaminobenzenes.

4. The substitution of chlorine or bromine for hydrogen in the benzene nucleus increases the developing energy. For example:



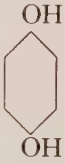
bromhydroquinone

or



chlorohydroquinone

are more active than



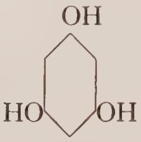
hydroquinone

5. The substitution of acid groups such as (COOH, SO_3H, etc.) for hydrogen in the benezene nucleus lowers the developing energy.

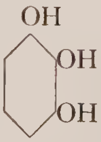
6. Developers with two hydroxyl groups (para and ortho hydroxybenzene) require an alkali. Developers with one hydroxyl and one amino group (paraminophenol, orthoaminophenol will develop without an alkali but are not practical when so used).

Compounds containing more than two active groups (OH, NH_2).

1. Substances containing three groups with a symmetrical arrangement (1:3:5) are not developers. No definite rule appears to apply to other groupings. For example:



1 : 3 : 5 hydroxybenzene
(not a developer)

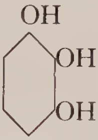


1 : 2 : 3 hydroxybenzene
(pyrogallol)

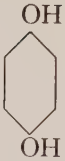
2. The energy of developing agents containing three hydroxyl or amino groups is greater than that containing two such groups.

Southworth—Developer Constitution and Toxicity. Brit. J. Phot. **85** (1938) 390.

For example:



is more energetic than

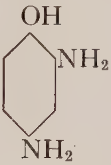


1 : 2 : 3 hydroxybenzene
(pyrogallol)

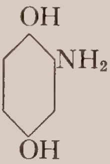
parahydroxybenzene
(hydroquinone)

3. Compounds containing three hydroxyl groups (Pyrogallol) can develop without an alkali but are not practical unless used with an alkali.

4. Increasing the number of amino groups increases the developing energy. For example:



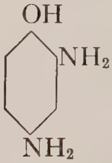
is more powerful than



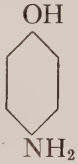
diaminophenol

monoamino parahydroxybenzene

5. If the developer contains three or more hydroxyl and amino groups, the energy is greater without an alkali than with a developer containing only two such groups. For example:



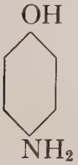
is more energetic without an alkali than



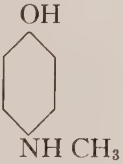
diaminophenol

paraminophenol

7. The energy of a benzene derivative which is already a developer is increased by the introduction of a methyl CH_3 group. For example: The energy of



is increased by the replacement of one H of the NH_2 by CH_3



paraminophenol

monomethylparaminophenol (metol)

The maximum reducing energy is obtained when the group is in the ortho position with respect to a hydroxyl.[4]

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[4] Seyewetz, A., *Le Negatif en Photographie*, 2d ed. p. 164.

Characteristics of the Principal Organic Developing Agents.—*Diaminophenol* (*Amidol*). Diaminophenol is one of the few developing agents in general use which does not require an alkali. With sodium sulfite alone it forms an energetic, soft-working developer which is employed chiefly for the development of bromide papers. Solutions of diaminophenol deteriorate rapidly and generally are inactive in from two to three days even if kept in tightly closed vessels. Deterioration is not accompanied by any marked change in color; hence, the appearance of the solution is no indication of its condition. The keeping properties of solutions of diaminophenol may be improved slightly by the addition of boric acid,[5] glycollic [6] or lactic [7] acid or tin chloride.[8]

Hydroquinone (*Hydrochinon, Hydrokinone, Quinol*). Hydroquinone, a developing agent of low energy, is quite sensitive to bromide and other restrainers, and its activity is greatly reduced by low temperatures, so much so that it is practically inert below 50° F. (10° C.). In negative development, the highlights appear first, then the middle tones and lastly the shadows. The tendency, therefore, is towards density and contrast rather than detail.

Hydroquinone is used alone chiefly for work in which extreme contrast and density are required. It may be used with either the alkaline carbonates or the caustic alkalis, although the latter are preferred for the highest possible density and contrast, while for certain materials, the use of paraformaldehyde is recommended.

For general purposes, it is usually combined with metol (monomethyl paraminophenol).

Chloro- or Brom-Hydroquinone (*Chloroquinol, Adurol*). As developers these substances are similar to hydroquinone but are more energetic, particularly at low temperatures, are less sensitive to bromide and other restrainers, and have less tendency to fog and stain. For negative development, they are usually used in combination with metol.

[5] Namias, *Prog. Foto.* (1921) 45.

[6] Crowther, *Brit. J. Phot.* **67** (1920) 642.

[7] Bunel, *Bull. Soc. franç. Phot.* (1921) 290.

[8] Desalme, *Brit. J. Phot.* **68** (1921) 359.

Druce—Stabilizing Solutions of Amidol. Brit. J. Phot. **69** (1922) 81.

Bramer and Zabriskie—Production of Hydroquinone. (Eastman Kodak Co.) U.S.P. 1,998,177 of 25.4.34.

Lobel and Bunel—Developer Containing Diaminophenol and *p*-Phenylenediamine in Bisulphite Solution. Bull. Soc. franç. Phot. **13** (1926) 143–147.

Glycin (*Athenon*). As a developer, glycin is slow but powerful. It is especially notable for the fine grain of the reduced silver and the freedom from any tendency to fog even in the absence of an alkaline bromide. Unlike other organic developing agents, glycin is not directly oxidized by air and does not produce a stain image. It keeps well in solution and is especially suited to continuous use in tanks. Glycin is frequently used in combination with metol, with paraphenylenediamine and with hydroquinone for warm-black tones on papers. Chemically, it is *p*-hydroxy phenylaminoacetic acid.

Monomethylparaminophenol (*Metol, Elon, Rhodol, Photol*). Metol alone, or in combination with hydroquinone, has been one of the most popular of all developers since its introduction by Hauff in 1891. It is a rapid, soft-working developer which is only slightly affected by the presence of bromide or other restrainers. It has a long useful life, and used alone it will develop a larger amount of sensitive material before becoming exhaused than any other agent.

While metol will develop without an alkali, it is generally used with the alkaline carbonates, although borax and other alkalis are employed for special purposes. At times, it is difficult to secure sufficient contrast with metol alone; hence, it is usually combined with hydroquinone. Other popular combinations are metol-glycin and metol-pyro.

Paraminophenol. The free base is only slightly soluble in water; hence, the hydrochloride or sulfate is generally employed. When used with the alkaline carbonates, paraminophenol forms a rapid, soft-working developer which is notably free from any tendency to produce development fog even at temperatures considerably above normal. Paraminophenol is for this reason especially suitable for high temperature development.

Highly concentrated paraminophenol developers of exceptional keeping properties may be prepared by adding paraminophenol hydrochloride or sulfate to a solution of potassium metabisulfite and adding sufficient sodium hydroxide to dissolve the precipitated free base. Developing preparations of this type have been available commercially for years; among the better known are Rodinal, Azol, and Actival.

Ermen—Rodinal Type Developers. Brit. J. Phot. **67** (1920) 611.

Gray—The Preparation of Concentrated Developing Solutions. Brit. J. Phot. **80** (1933) 175.

Schering—Benzyl Para-amidophenol Compounds as Developers. British Patent 20,050 (1907).

Willcock—Concentrated Phenolate Developers. Brit. J. Phot. **83** (1936) 256–257.

Paraphenylenediamine. The developing properties of paraphenylenediamine were discovered by A. and L. Lumière and A. Seyewetz who recognized its value as a fine-grain developer.[9] The fine grain is due (1) to its solvent action on silver halide and (2) its low reduction potential. These two factors prevent full development of the latent image thus necessitating an increase in exposure as compared with more energetic developers such as paraminophenol and diaminophenol. It is possible that development with paraphenylene diamine is largely of the character associated with physical development in which silver is deposited on the latent image from a silver-bearing solution.

The silver deposit is dichroic, i.e., black by transmitted light and cream-colored by reflected light so that a thin negative frequently appears positive by reflected light. The printing density, however, is greater than the visual density so that negatives which appear to be lacking in density and contrast may be of good printing quality.

The free base, $C_6H_4(NH_2)_2$, is slightly alkaline and may be used without an alkali; the hydrochloride, $C_6H_4(NH_2)_2 \cdot 2HCl$, however, is acid and must be used with an alkali in order to develop. The hydrochloride oxidizes less readily than the free base and is more soluble in cold water although less so in hot water. Both keep well in the dry state if protected from the air.

Paraphenylenediamine (free base) is supplied under many trade names such as Paramine, Diamine, Diamine P. Dianol, etc., and the hydrochloride as P.D.H., Diamine H. etc. Both are toxic and produce painful skin eruptions on those susceptible. For those affected by

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[9] *Bull. Soc. franç. Phot.* **20** (1904) 422.

Bramer and Ruggles—Process for Preparing Metol. Kodak Ltd. B.P. 435,721 (10.11.33).

Emmermann—Pyrogallol Monomethylether as Developing Substance. Phot. Ind. **36** (1938) 1085.

Ermen—Preparation of Monomethyl Paramidophenol Sulphate (Metol). Phot. J. **63** (1923) 223.

Hubl—Metol-Quinol Developer. Phot. Rund. **63** (1926) 481–487.

Reinders and Beukers—Metol-Hydroquinone Developers. Phot. J. **74** (1934) 78.

Lehmann and Tausch—Chemistry of Metol-Quinol Development. Phot. Korr. **71** (1935) 17, 35.

Tschibissoff and Tschelzoff—Chemistry of Developers and Development. II. Metol-Quinol Developers and Metoquinone. Kinotech. **11** (1929) 315–321.

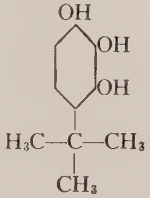
Whitaker—Manufacture of Monomethyl Para-Aminophenol and its Sulphate. (Industrial Dyestuff Co.) U.S.P. 1,993,253 of 18.9.34.

paraphenylene, the use of rubber gloves appears to be the only preventative.

Pyrogallol. Pyrogallol has been in use longer than any other organic developing agent; however, it has a number of disadvantages which cause it to be used less and less. It oxidizes readily and the yellow oxidation product stains the gelatin so that the useful life of a pyrogallol developer is short. In development the oxidation taking place in the reduction of the exposed silver halide to metallic silver results in the formation of a stain image. Most developers produce a stain image but with none of the common developing agents is the stain image as intense as with pyrogallol. Its existence can be demonstrated by reducing a portion of a pyro developed negative in Farmer's reducer. This removes the silver image, leaving a yellow image which is composed of the oxidation product formed in the process of development. The intensity of the stain image depends on the amount of sodium sulfite or other preservative used, the amount of solution exposed to air, the temperature, and the degree of agitation. It is difficult to control all these factors precisely, and therefore, the intensity of the stain image; hence, since the density and contrast of the negative vary with the stain image, it is difficult to secure as uniform results with pyrogallol as with other developing agents.

Pyrogallol is usually employed with the alkaline carbonates as an alkali; in the presence of diaminophenol, however, pyrogallol is capable of developing without an alkali.[10]

[10] Hall, *American Photography* (1922) 326; Bunel, *Bull. Belge Phot.* **44** (1922) 151. A number of methylated, ethylated, or other substituted pyrogallols have been patented. *Rubinol,* a product of the Defender Photo Supply Co., of Rochester, N. Y., appears to be monotertiary butyl pyrogallol.



Pyrogallol-dimethylaniline—Bayer, B.P. 10,721.
Pyrogallol-methylether-monoglycollic acid—Agfa, D.R.P. 155,568.
Pyrogallol-1-monoethylether—Schultes, U.S.P. 2,017,295.
Monomethyl-pyrogallol—Stockelbach, U.S.P. 2,037,742.

Lowe—Paraphenylenediamine: Free Base or Hydrochloride? Zeiss Magazine **2** (1936) 43, 58, 75 and 78.

Pyro is a very flexible developing agent, much more capable of modification than some of the agents which have largely replaced it. With concentrated solutions, strong contrast may be obtained while with more dilute solutions and a lower concentration of alkali, soft, delicate results are produced. Pyro is perhaps most often used alone; frequently, however, it is combined with metol or with glycin.

Minor Developing Agents.—The following developing agents are (1) little used, (2) used only for special purposes or (3) are no longer available commercially.

Edinol. As a developer, Edinol is similar to metol but less energetic. It is noticeably free from staining and fogging tendencies. It may be used alone, but is more generally employed in combination with hydroquinone. It is now seldom employed except by those affected by metol. Chemically, Edinol is *o*-hydroxymethyl *p*-aminophenol.

Eikonigen. This developer is no longer available commercially, having been replaced by metol which it resembled in many respects, its principal differences being its lower energy and more rapid exhaustion in use. Chemically, Eikonigen is 1-amino-2-naphthol-6-sulfonic acid.

Ortol. Used alone, ortol bears a close resemblance to pyro, not only as respects the color of the image, which is brownish-black, but in the progressive appearance of the image. As with pyro, the highlights appear first, followed by the half-tones, and lastly the shadows. This gradual building up of the image is quite different from the action of metol and other rapid developers in which the highlights, half-tones, and shadows appear at very nearly the same time, and density is built up later. Ortol, however, does not stain and keeps better in solution. Chemically, it is *o*-aminophenol sulfate and hydroquinone.

Pyrocatechin (*Kachin*). Pyrocatechin is a more energetic developer than hydroquinone, to which it is closely related chemically. It

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Weinland—*p*-Phenylenediamine—the Chemical. Camera (Phila.) **49** (1934) 145.

Seyewetz—Use of *o*-Phenylenediamine for the Development of Fine-grain Images. Bull. Soc. franç. Phot. **23** (1936) 159.

Jacobsohn—Properties of the Pyrogallol Developer. Kinotech. **II** (1929) 76.

Schultes—New Developers Derived from Pyrogallol. Phot. Ind. **34** (1936) 896; Sci. et Ind. Phot. **7** (1936) 344.

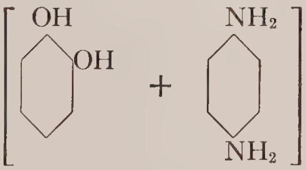
Seyewetz—Combination of Developers of Phenolic Function with those of Amine Function. New Combination of *o*-Phenylenediamine and Pyrocatechol. Bull. Soc. franç. Phot. **23** (1936) 253.

differs from other common organic developing agents in retaining its normal developing power in the presence of hypo. This property has caused it to be used in processes of combined developing and fixing. Pyrocatechin (Catechol) is 1-2 dihydroxy benzene.

Metoquinone and Chloranol. These are two introductions of A. and L. Lumière.[11] Metoquinone is a chemical combination of methylparaminophenol (metol) and hydroquinone and chloranol a combination of paraminophenol and chloro-hydroquinone. Unlike the parent substances both develop without an alkali. In this and many other respects, they are similar to diaminophenol, but unlike it are quite stable in use. Except for Lumière products, such as the Lumière Autochrom, neither is in general use. Pyramidol, a condensation product of paraminophenol and hydroquinone, was introduced by Hauberrisser. It was similar to paraminophenol and is no longer available commercially.

Duratol, Monomet, Neol, Hydramine. These are all no longer obtainable. Duratol (Benzyl paraminophenol) was introduced by Schering in 1910 as a substitute for methylparaminophenol, as was monomet (paraminothocresol hydrochloride) introduced by the White Band Company in 1916. Neol (paraminosalicylic acid) was introduced by Hauff in 1918 as a compensating developer permitting the correction of considerable overexposure.[12] Hydramine, a condensation product of hydroquinone and paraphenylene diamine, was introduced by A. and L. Lumiere in 1899.

A combination of pyrocatechin and paraphenylenediamine was introduced by Johnson Ltd. of London, for fine grain development under the trade name of *Meritol.*[13]



Reduction Potential of Developing Agents.—The relative reducing energy of a developing agent is known as its *reduction potential.* The reduction potential of a developing agent may be determined in one of three ways:

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[11] *Bull. Soc. franç. Phot.* (1903) 231.

[12] B.P. 154,198 of 1918. Lüppo-Cramer, *Phot. Korr.* (1920) 270.

[13] Starnes, B.P. 466,626.

1. *The amount by which density is depressed with a given quantity of a restrainer such as potassium bromide.* For a given concentration of potassium bromide, under fixed conditions of development, the amount by which the density is reduced, or depressed, will depend upon the ability of the developer to overcome the resistance of the soluble bromide. Developing agents of high energy will, under the same conditions, require larger amounts of potassium bromide to produce a given reduction in density than those of lower energy, hence the concentration of bromide required to produce a given depression in density will be in direct proportion to the energy, or reduction potential, of the developing agent. This method of measuring the relative reduction potential of developing agents appears to have originated with Sheppard[14] and has been more widely used than either of the others about to be described.

2. *The amount of silver bromide reduced to silver by a given quantity of the developing agent.* By this method a given quantity of the developer is added to silver bromide, formed by precipitation in water, and the reduced silver is collected and measured. The reduction potential of the developing agent is then expressed in terms of the quantity of metallic silver produced from the reduction of silver bromide. This method, apparently the first to be employed, was originated by Andresen[15] but has never been widely used.

3. *Electrometric Methods.* The possibility of measuring the reduction potential by developers by electrometric methods was indicated by Oswald,[16] who called attention to the analogy with Ohm's law.

Electrometric methods have been utilized by Bredig, Matthews and Barmeier, Frary and Nietz and more recently by Evans and Hanson. The results obtained by the latter are quite different from earlier measurements made by the density depression method as will be evident from the following table in which the values from the density depression method, used by Nietz, are compared with those obtained by the electrometric method; the potentials given being measured against the standard saturated calomel reference cell.[17]

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[14] Sheppard, *J. Chem. Soc.* (London) **39** (1906) 530.

[15] Andresen, *Phot. Korr.* **35** (1898) 447. Valenta, *Photographische Chemie und Chemikalien-Kunde,* II, 506, Wm. Knapp, Halle a/S.

[16] Oswald, *Outlines of General Chemistry.* Macmillan 1890.

[17] Evans and Hanson, *J. Phys. Chem.* **41** (1937) 509.

	REDUCTION POTENTIAL	
Developing Agent	*Density Depression Method*	*Electrometric Method*
Diaminophenol	30	-0.434
Bromhydroquinone	21	-0.327
Monomethylparaminophenol sulfate	20	-0.308
Pyrogallol	16	-0.388
Dimethylparaminophenol sulfate	10	-0.293
Chlorhydroquinone	7.0	-0.335
Paraminophenol (HCl)	6.0	-0.291
Toluhydroquinone	2.2	-0.390
Hydroquinone	1.0 (standard)	-0.357
Paraphenylene diamine	0.3	....

The outstanding difference in the values obtained by the two methods is the much higher potential of hydroquinone with the electrometric method than with the older density depression method. It will be observed that the potential of hydroquinone, as measured by the electrometric method, is higher than that of monomethylparaminophenol (metol), while the difference in potential is greater, and in the opposite direction, when measured by the depression of density. The potentials, as measured electrometrically, do not correspond very well with the observed differences in the rate of development, or velocity constant, but are in fair agreement with the maximum densities obtainable with the various developing agents.

Solubility of Developing Agents.

Agent	*Solubility in Water at 60° F. (15° C.)*	*Solubility in 5% Na_2SO_3 and Na_2CO_3*
Diaminophenol	1 in 4	
*Edinol	15.9 gm. per liter	9.7 gm. liter
*Eikonigen	7.6 “ “ “	8.2 “ “
*Glycin	0.23 “ “ “	12.8 “ “
*Hydroquinone	5.7 “ “ “	7.4 “ “
*Metol	4.8 “ “ “	4.5 “ “
*Paraminophenol (base) HCl	33.0 “ “ “	3.2 “ “
*Pyrocatechin	33.3 “ “ “	35.7 “ “
*Pyro	52.4 “ “ “	41.8 “ “

* Kail, *Phot. Korr.* 1921, Festnummer.

Keeping Properties of Developers in Solution.—The keeping properties of a developing solution depend upon the developing agent, the concentration of sulfite, and in certain cases, as with pyrogallol, the acidity of the solution. No investigations of the rate of oxidation with

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Evans and Hanson, Jr.—Reduction Potential and the Composition of an M.Q. Developer. J. Soc. Mot. Pict. Eng. **30** (1938) 559.

different developing agents using a constant concentration of sulfite appear to have been made. Milbauer[18] studied the rate of oxidation of various developing agents using typical formulae. The order of stability was found to be as follows: glycin (best), chloro-hydroquinone, metol, eikonigen, ortol, hydroquinone, diaminophenol and lastly pyrogallol.

The rate of deterioration of developing solutions was studied also by Hubl[19] who placed the different agents in the following order: metol-hydroquinone (best), glycin, pyrocatechin, chloro-hydroquinone, metol, hydroquinone, and lastly pyrogallol.

Differences among Developing Agents with Respect to Threshold Speed.—The various developing agents differ in the minimum light exposure rendered visible upon development. Of the common organic developing agents, methylaminophenol (elon, metol, etc.) results in the highest threshold speed and pyrogallol, the lowest. In general, the order in which developing agents are placed in this respect is the same as their reduction potential and it is possible that there is some connection between the two.[20]

The difference between developing agents is largely independent of the composition of the developer. The differences are more marked in the case of process and positive materials than with those of higher speed.

Differences in Developing Agents as Respects Fogging Properties.—The fog characteristic of a developer may be defined as the ratio of the rate at which the image is developed and that at which fog appears.[21]

The fog characteristic depends upon so many factors that it is difficult to determine values for the developing agents directly except under certain narrowly defined conditions which in many cases are not directly applicable to those of practical photography. In general, however, it may be said that there appears to be no connection between the fog characteristic and the reduction potential of a developing agent. Thus hydroquinone, pyro, metol and diaminophenol represent a series with increasing reduction potential, but with fogging tendencies in the reverse order.[22] Paraminophenol is exceptionally free from any tendency to produce fog even at high temperatures. According to Scheberstow, it has the lowest fog ratio of any of the organic developing agents in general use. It is probable that the fogging tendencies of some developing agents are increased by the impurities found in the commercial product and by oxidation products which in some cases tend to produce fog.[23]

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[18] *Phot. Korr.* **54** (1917) 232.

[19] *Entwicklung der photographischen Bromsilbergelatineplatten,* W. Knapp, Halle a/S 1922.

[20] Bullock, *Sci. Ind. Phot.* **6M** (1926) 33, 41; **7** (1927) 5, 9.

[21] Sheberstov, *Sci. et Ind. Phot.* **6** (1935) 298. Sheberstov, *Bull. Soc. franç. Phot.* **22** (1935) 209.

Mees and Piper found that fog is practically independent of the concentration of alkali—a conclusion at variance with the commonly accepted opinion—but increases rapidly with an increase in the concentration of sulfite up to a maximum, which varies with different developing agents. Beyond this point, the increase is slight. The tendency of a developer to produce fog almost invariably increases with the dilution owing to the increased oxidation which results in aerial or oxidation fog.[24]

Differences in Developing Agents with Respect to Rate of Exhaustion.—With all developing agents, there is a loss in activity with use. This loss in activity affects development in two ways: (1) longer development is required to reach a given degree of contrast or gamma, and (2) the lower densities are less fully developed tending to produce the effect of underexposure.

The effect of repeated use on density with different developing agents using a standard formula was investigated by Strauss who found that [25] metol has the longest useful life, followed in order by paraminophenol, edinol, ortol, chloro-hydroquinone, glycin, pyrocatechin and, much worse than the others, pyro.

Ermen investigated the exhaustion of developers using the time of appearance on developing papers.[26] His results placed the different developing agents in the following order: metol (best), dimethylaminophenol, paraminophenol, metol-chlorohydroquinone, chloro-hydroquinone, and lastly hydroquinone.

Identification of the Principal Developing Agents.—Methods of identifying the various organic developing agents have been described

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[22] Nietz, *Theory of Development,* Van Nostrand 1922.

[23] Crabtree, "Chemical Fog," *American Annual of Photography,* 1919.

[24] Mees and Piper, **51** (1911) 226; **52** (1912) 221.

[25] *Phot. Ind.* (1925) 309.

[26] *Brit. J. Phot.* **68** (1921) 64.

Dundon and Crabtree—Fogging Properties of Developers. Brit. J. Phot. **71** (1924) 701, 719.

by Andresen,[27] Clarke,[28] Ermen,[29] Lehrman and Taush,[30] Plauman[31] and by Huse and Atkinson.[32] The accompanying table is from the last mentioned paper.

IDENTIFYING REACTIONS OF DEVELOPING AGENTS

Agent	*Ferric Chloride (in Acid Solution)*	*Benzaldehyde (in Alkaline Solution)*	*Sodium Nitrite (in Acid Solution)*
Elon (M.P. Elon base, 85° C.)	Purple color develops slowly in cold	No ppt. if pure	Colorless, needles slightly soluble in water, M.P. 136° C.
Glycin (M.P. 200° C.)	Darkens slowly in cold	No ppt.	No ppt.
Amidol (M.P. base, 79° C.)	Bright red color immediately	Dirty yellow ppt. M.P. indeterminate	Dark brown ppt.
P-amino phenol (M.P. base, 184° C.)	Purple color develops slowly in cold	Yellow ppt. M.P. 183° C.	Red color with R-acid
P-phenylene diamine (M.P. base, 140° C.)	Green-blue, changing immediately in brown	Yellow ppt. M.P. 138° C.	Red color with R-acid

The Preservative.—All organic developing agents have a strong affinity for oxygen. It is necessary, therefore, to add an antioxidizing agent, or preservative, which is usually sodium sulfite, $NaSO_3$ (dessicated), or $Na_2SO_3.7H_2O$ (crystal). Sodium sulfite is occasionally replaced wholly, or in part, by sodium bisulfite, Na_2HSO_4, which in an

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[27] Andresen, Valenta, *Photographische Chemie und Chemikalienkunde,* Knapp, Halle a/S.

[28] Clarke, *J. Ind. & Eng. Chem.* Nov. 1918; *Brit. J. Phot.* **65** (1918) 499.

[29] Ermen, *Brit. J. Phot.* **64** (1917) 390.

[30] Lehrman and Tausch, *Phot. Korr.* **71** (1935) 17, 35.

[31] Plauman, *Phot. Ind.* **29** (1931) 341.

[32] Huse and Atkinson, *The Chemical Analysis of Motion Picture Developers and Fixing Baths.* Motion Picture Film Division, Eastman Kodak Co., Hollywood, Calif.

EVANS AND HANSON, JR.—Chemical Analysis of an M.Q. Developer. J. Soc. Mot. Eng. **32** (1939) 307.

SOUTHWORTH—Acid Sulphites versus Normal Sulphites in Developers. Brit. J. Phot. **85** (1938) 262.

TULL—Oxidation of Stock Sulphite Solutions. Brit. J. Phot. **85** (1938) 135.

alkaline solution is converted into sodium sulfite and sodium bicarbonate.

The addition of sulfite (1) protects organic developing agents against aerial oxidation; (2) tends to prevent the formation of staining developer products; (3) acts as a silver halide solvent by the formation of complexes, and (4) is a weak alkali and under certain conditions increases the rate of development and the maximum density obtainable.

The reactions involved are not precisely known but it appears from the work of Andresen,[33] Pinnow,[34] Rzymkowski,[35] Seyewetz and Szymson,[36] Lehrman and Tausch,[37] and Evans and Hanson [38] that the chief product is a monosulfonate of the developing agent. This appears to be formed in two steps which may not be the same for all developing agents. The intermediate compound, however, is an oxidized form of the developing agent which then reacts with the sulfite to form the monosulfonated compound. In the opinion of Evans and Hanson, "the primary action of sulfite in a developer solution is that of an acceptor for the oxidized form" of the developing agent.

As a solvent of silver halide, sodium sulfite is used in a relatively high concentration in so called " fine grain " developers. The solvent action, which is at its greatest with silver chloride and relatively insignificant with silver iodide, acting upon the surface of the grains of silver halide prevents them from attaining their full size in development and reduces the tendency of the grains in close proximity to one another from merging to form larger aggregates of silver.

The addition of sulfite to an alkaline solution of certain developing agents, particularly hydroquinone, paraminophenol, and metol, affects the rate of development and particularly the maximum density. Evans and Hanson have shown that this may be explained as being due to the increased potential of the solution, an increase in the potential of the solution resulting in an increase in the maximum developable density.

The quantity of sulfite employed varies greatly; among the factors determining the amount required are:

1. *The susceptibility of the developing agent, or agents, to oxidation.* Developing agents vary considerably in resistance to oxidation, ranging from pyrogallol, which in an aqueous solution is completely oxidized

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[33] Andresen, *Eder's Handbuch,* 6th Ed. (1930) vol. 3.

[34] Pinnow, *Z. Elektrochem.* **21** (1915) 380.

[35] Rzymkowski, *Phot. Ind.* (1928) p. 627.

[36] Seyewetz and Szymson, *Bull. Soc. franç. Phot.* **21** (1934) 71, 236.

[37] Lehrman and Tausch, *Phot. Korr.* **71** (1935) 17, 35.

[38] Evans and Hanson, *J. Phys. Chem.* **41** (1937) 509.

within a few hours, to glycin which is oxidized only very slowly. The more readily the developing agent accepts oxygen from the air, the greater the amount of preservative required for satisfactory keeping properties in solution.

2. *The concentration of the developer.* The amount of preservative required for a dilute developer is greater than for a more concentrated solution because the proportion of the developing agent to the available oxygen is less, thus rendering necessary an increased amount of the preservative to insure satisfactory keeping properties.

3. *The temperature at which the developer is kept.* The rate of oxidation increases with the temperature; consequently, a developer used at a temperature above normal requires a larger amount of preservative.

4. *The keeping properties required and the way in which the solution is used.* Developers which are used once in a tray and then discarded naturally do not need to keep so well as those designed for use in tanks over a long period of time. On the other hand, the conditions under which the developer is used may favor rapid oxidation of the solution. The amount of oxidation, for example, is relatively greater in tray development than in a tank because a larger proportion of the solution is exposed to air. In certain of the processing machines used in motion picture film processing and photo-finishing, film is exposed to the air for some time in transfer from one tank to another or in passing over loops above the surface of the solution. In such cases, an increased amount of the preservative is required to prevent rapid oxidation of the developer and oxidation fog.

5. *The alkalinity of the solution.* The more strongly alkaline the developer, the more rapid the rate of oxidation; for satisfactory keeping properties it is necessary, therefore, to use an increased amount of preservative. Under given conditions, a larger amount of preservative is required with the caustic alkalis than with alkaline carbonates.

Insufficient amounts of the preservative result in rapid oxidation of the developer causing (1) a loss in developing power, (2) the formation of colored oxidation products which stain the gelatin and (3) oxidation fog.

Large amounts of the preservative improve the keeping properties of the developer but increase the time of development and reduce the effective emulsion speed through the solvent action on silver bromide.

The Alkalis.—The alkalis commonly employed in organic developers are the alkaline carbonates (sodium and potassium carbonate), the caustic alkalis (sodium, potassium, ammonium and lithium hydroxide), and for special purposes the basic phosphates (sodium tribasic phosphate), the borates and metaborates. Other substances less frequently employed include acetone, formaldehyde, paraformaldehyde or trioxymethylene, trimethylamine, trimethylanolamine, sodium metasilicate and salicylic acid. Some of these are not alkalis in the usual sense but disassociate in solution and combine with the sulfite and the developing agent to produce the necessary alkali. With acetone and hydroquinone, for example, the reaction is probably

$$\begin{aligned}&2CH_3.CO.CH_3 + 2Na_2SO_3 + C_6H_4.OH.OH \\ &\qquad = 2(CH_3.CO.CH_3NaHSO_3) + C_6H_4.ONa.ONa.\end{aligned}$$

In other words, the acetone results in the disassociation of the sodium sulfite into sodium bisulfite and sodium hydroxide.

The evidence available indicates that for any particular developing agent the rate of development is very largely, if not wholly, a function of the pH of the solution. The particular alkali appears to be immaterial, so long as the quantity used results in a solution of the same pH value.[39]

The substitution of one alkali for another on the basis of molecular weight will not, therefore, result in a developing solution of the same energy unless the substitution results in a solution having the same pH value.

Each developing agent has its own pH limits within which it may be used practically as a developer. Metol (Monomethylparaminophenol), for example, is an active developer at a pH of 6, while hydroquinone is practically inactive, requiring a solution pH of about 9. The activity increases with increased solution pH much more rapidly, however, in the case of hydroquinone than with metol, both displaying an equivalent activity at a solution pH of approximately 10.5.[40]

[39] Exceptions should be noted in the case of the basic phosphates (Burki and Ostwald, *Helv. Chim. Acta* **22** (1939) 30); and the Borates (i.e., Borax) in the case of certain developing agents, namely, pyro and pyrocatechin (Reinders and Beukers, *Phot. J.* **74** (1934) 78).

[40] Reinders and Beukers, *Phot. J.* **74** (1934) 78; Stenger and Mutter, *Phot. Ind.* **31** (1933) 712, 736, 760, 777.

GROVES—Alkali Substitutes in Developers. B.P. 488,374 (1937).

SEYEWETZ—Use of Hexamethylenetetramine in Photographic Developers. Bull. Soc. Franc. Phot. (iv) **I** (1939) 85.

WILLCOCK—Trioxymethylene (in Developers). Brit. J. Phot. **86** (1939) 195.

The alkali in widest use is undoubtedly sodium carbonate, desiccated (Na_2CO_3) or monohydrate ($Na_2CO_3 . H_2O$). Potassium carbonate (K_2CO_3) owing to its greater solubility, is more suitable for concentrated stock solutions but is not widely used because of its higher price. The caustic alkalis are used chiefly in developers designed for use with process materials employing developing agents of low energy, such as hydroquinone. In general, developing solutions containing caustic alkalis are exhausted more rapidly with use than those with the fixed alkalis, such as sodium carbonate.

Borax, the tribasic phosphates, and other substances mentioned in the first paragraph of this section, with the exception of formaldehyde and paraformaldehyde, are used chiefly in the so-called "fine grain" developers. The use of paraformaldehyde (trioxymethylene) is restricted practically to developers designed for the specialized sensitive materials employed in photomechanical reproduction processes.

Effect of an Alkaline Bromide in Development.—The presence of an alkaline bromide, such as potassium bromide, lowers the degree of ionization of silver bromide, and by reducing the concentration of silver cations restrains development. The effect of an alkaline bromide on development is shown in Fig. 208. It is evident that with increased times of development not only the slope of the straight-line portion of the $D \log E$ curve increases but that it shifts towards the left so that speed increases with the gamma.

The restraining effect of an alkaline bromide is more marked with developers of low energy, such as hydroquinone, than with the more energetic, such as metol. The depression in density resulting from an alkaline bromide is for any particular developing agent approximately proportional to the logarithm of the bromide content and is equivalent practically to reducing the effective speed of the emulsion. The effect, however, becomes less marked as the time of development is increased.

An alkaline bromide is added to developing solutions chiefly for the purpose of preventing fog. The restraining effect of bromide is greater on fog than on the latent photographic image; however, since modern negative materials almost invariably contain free bromide, and restraining substances are formed in the process of development, a restrainer is omitted in many developing formulas and the solution "conditioned" before use by developing waste film, or by adding a small quantity of used developer. The restraining products added in this manner are more effective in preventing fog than is potassium bromide.

A number of organic substances have been discovered which, for a given depression of density, are more effective in preventing fog than is potassium bromide. These, however, have not come into general use.[41]

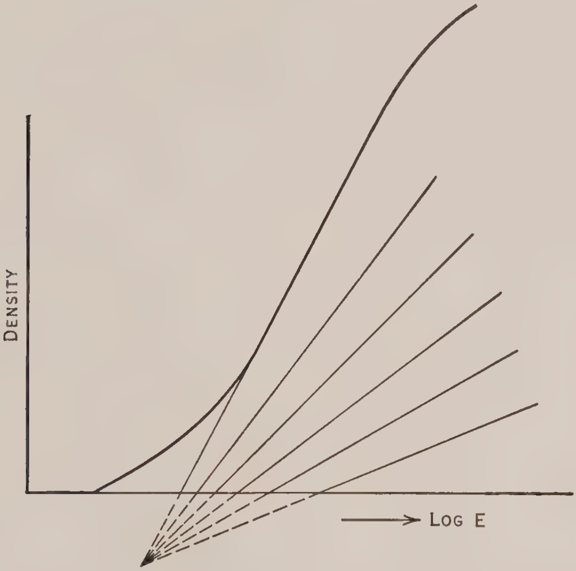

FIG. 208. Effect of an Alkaline Bromide on Development.

The restraining effect of bromide on fog enables development to be carried to a higher contrast; hence, to obtain the highest possible contrast in any particular emulsion, a comparatively high concentration of bromide is an advantage. This is particularly the case with sensitive materials of the process type.

Effect of Use on Developing Solutions.—With use, a developing solution becomes slower in action as a result of (1) depletion of the developing agent, or agents, and (2) the restraining effect of by-products of the process of development in the form of sodium bromide, sodium iodide, and developer oxidation products. Some of the sulfite is used up in combining with the oxidation products of the developing agent, but in view of the relatively large quantity of sulfite present in most developers, the decrease is insignificant. Only a small part of the total quantity of alkali is used up in development.

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[41] Trivelli and Jensen, *J. Franklin Inst.* **210** (1930) 287; (1931) 155. Wulff, U.S.P. 1,696,830. Citrates, tartrates and boro-tartrates act similarly to potassium bromide. Lobel, *Bull. Soc. franç. Phot.* (1928) 167.

The by-products of development which accumulate in a used developing solution retard development and increase the time of development necessary for a given density and contrast. If present in more than a limited amount, development is so greatly restrained as to reduce the density of the highlights and shadows of the image even upon prolonged development, resulting practically in a loss in effective emulsion speed. A used developer, therefore, is incapable of getting the most out of an exposure, and a normally exposed image developed in a used solution appears to be underexposed.

In general, developing agents, such as metol, with a high reduction potential are less sensitive to the restraining effect of developer by-products than those of low potential such as hydroquinone and glycin.

The loss in density and contrast due to partial exhaustion of the developing solution may be overcome to a certain extent by the addition of a replenishing solution, which may be either a solution of the same composition as the original formula, but without bromide, or a more concentrated solution containing a larger proportion of the developing agent, or agents, and alkali. It is not possible, regardless of the composition of the replenishing solution, or the conditions of replenishment, to bring a partially exhausted developing solution back to its original condition. However, with suitable replenishment the period over which a developing solution may be used without involving an excessive loss in the density and contrast of the image may be greatly extended.

In motion-picture processing, where the technique of developer replenishment is most highly advanced, the developing solution is usually circulated through a large auxiliary storage tank and a certain proportion of the total volume is replaced constantly with fresh solution. In some cases, however, fresh developer is allowed to flow into the developing tank near the point at which the undeveloped film enters and the partially exhausted developer is drawn off from the point where the film leaves the developing tank. Experiments have shown that if

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Lobel and Lefevre—Action of Citric Acid on Metol-Quinol Developer. Bull. Soc. franç. Phot. **14** (1927) 48–50.

Lobel—Tartrates and Boro-tartrates as Restainers. Sci. et Ind. Phot. Inf. Cine. **8** (1928) 73.

Staud and Dundon—Photographic Developer Containing an Antifogging Agent. (Eastman Kodak Co.) U.S.P. 2,080,017 of 5.7.35.

development is begun in a fresh solution, the film may be transferred to a partially exhausted solution as soon as the shadow detail has appeared, without loss of effective exposure. In other words, once the detail in the shadows has appeared, a partially exhausted solution is capable of building up the density and contrast required for good negative quality.

In small-scale processing the usual method is to maintain the level of the solution in the tank through the addition, from time to time, of a replenishing solution which contains sufficient of the developing agent, or agents, and alkali to offset the restraining action of the developer reaction products. Only sufficient sulfite need be added to insure satisfactory keeping properties of the replenishing solution.

By adding sufficient replenshing solution to maintain the level of the developing solution in the tank, the replenishing solution added is equal in volume to that of the developer which has been removed from the tank on the sensitive material. This in turn is directly proportional to the amount of material processed; hence, the amount of replenishing solution added is directly proportional to the amount of sensitive material which has been developed.

The only satisfactory method of determining the best formula and the amount of replenishing solution required is by actual photographic tests made by developing sensitive material under known conditions.

Testing the Condition of a Developing Solution.—One of the most satisfactory methods of determining the condition of a developer is to secure a number of test negatives which have all received the same exposure and develop one of these for the average time in the fresh solution as a standard. Tests of the condition of the developing solution may be made from time to time by developing one of the negatives and comparing it with the standard. When it is evident

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ALBURGER—Mathematical Expression of Developer Behavior. J. Soc. Mot. Pict. Eng. **35** (1940) 282.

BAUMBACH—Chemical Analysis of Hydroquinone, Metol and Bromide in a Developer. J. Soc. Mot. Pict. Eng. **33** (1939) 517.

BLANEY—Method of Removal of Excess Halides from Photographic Developing Baths. U.S.P. 2,073,621 of 6.10.33.

EVANS—Maintenance of a Developer by Continuous Replenishment. J. Soc. Mot. Pict. Eng. **31** (1938) 273

HARVEY, WOOSLEY AND BAINES—Exhaustion and Regeneration of Developers. Proc. Ninth Int. Congress of Phot. Paris 1935. Sci. et Ind. Phot. (II) **6** (1935) 300.

WEISBERG (GREENWALD)—Regeneration of Photographic Developer Solutions. U.S.P. 2,073,664 of 9.9.33.

that there is a loss in negative density and shadow detail, the solution should be replenished. The amount of replenisher necessary may be determined by developing another test negative for the standard time. The amount of the replenisher solution added should be sufficient to produce with this standard time of development a test negative which matches the standard.

The supply of test negatives required for testing the condition of the developing solution is conveniently made by contact printing from a master positive.

A variation of the above method consists in developing a standard exposure for a definite time, stopping development instantly with a stop bath containing acetic acid and potassium iodide and comparing the image so obtained with a previously prepared standard. The composition of the stop bath is as follows:[42]

Potassium iodide	20 gm.
Glacial acetic acid	20 cc.
Potassium alum	40 gm.
Sodium sulfite	1 gm.
Water to make	1 liter

The acetic acid instantly stops the action of the developer and the iodide converts the undeveloped silver bromide to silver iodide which is not darkened by light. The alum serves to harden the film and the sulfite prevents the solution from becoming colored because of the action of light on the potassium iodide. The bath can be used repeatedly as long as it remains acid.

The method of making the test is as follows: A strip of film or bromide paper containing a standard exposure, preferably a print from a step-tablet, is quickly dipped into the developer and the time noted. While in the developing solution, it should be kept in motion to prevent non-uniform development. When testing a fresh solution the strip should be examined from time to time and removed from the developer when all except the last exposure step is visible. This time constitutes the standard. The strip should be removed immediately and placed in the stop bath. It may be examined in a bright light within 10 to 15 seconds after having been placed in the stop bath.

To determine the degree of exhaustion of a developing solution, a similar test strip should be developed for the standard time and, after immersion in the stop bath, compared with the strip developed in a fresh solution. The loss in density and shadow detail is easily seen.

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[42] Dundon, Capstaff and Brown, *J. Soc. of Mot. Pict. Eng.* **14** (April, 1930) 389.

The advantage of the dip test is that little time is required—three or four minutes being sufficient—and the differences are more readily seen than in a developed and fixed negative. With a little experience, a mere glance at the test strip is usually sufficient for an exact comparison.

Effect of Dilution on Developers.—Slight dilution of the developer affects principally the time of development and its fogging tendencies; with greatly diluted developers the character of the image is modified and it is not possible to obtain the same result as with an appropriate time of development in a more concentrated solution.

Very dilute developers produce images of soft gradation and, generally speaking, it is not possible to obtain images of the same vigor and density as with concentrated solutions however much the time of development may be increased. With an extremely weak solution, development is confined more or less to the upper layers of the emulsion, due to the exhaustion of the developer in penetrating the emulsion and the restraining influence of the by-products of development.

Extremely dilute developers are capable, therefore, of developing more or less completely the shadow portions of the image, but are incapable of developing the highlight areas fully and thus lead to negatives of soft gradation. Certain practices of development employed for obtaining images of soft gradation from contrast subjects make practical applications of this principle. (See page 548.)

The time of development for a given contrast (gamma) is not directly proportional to the dilution, except in the case of developing agents which are not directly oxidized by air. The only important example of a developing agent which is not oxidized directly is glycin, and with glycin developers the time is almost directly proportional to the concentration of the developer, except when considerably diluted. With organic developing agents other than glycin, the oxidation occurring within the solution results in the concentration of the developing agent being less than that indicated by the degree of dilution. Hence, the time of development, for the same negative contrast (gamma), is not directly proportional to the dilution, but is somewhat greater, depending upon the developing agent and the conditions of development.

While there appears to be no direct relationship between the concentration of the developer and its fogging tendencies, fog tends to

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Crabtree—Photographic Methods of Testing Developers. American Annual of Photography (1922) p. 184.

increase both with highly concentrated or with extremely dilute developers. The increased fogging tendency of dilute developers is probably due to oxidation fog.

Effect of Temperature on Development.—The effect of a given change in temperature on the time of development for a constant gamma is termed the *temperature coefficient.* The temperature coefficient represents the difference in the time of development for a constant gamma at a temperature difference of either 10° C. or 18° F. The temperature coefficient depends chiefly upon the developing agent; but variations in the proportion of alkali to the developing agent, the nature of the alkali, and the amount of soluble bromide present in the developer have to be considered in determining the temperature coefficient for any particular developing formula.

The temperature coefficients of a few of the more common developing agents are as follows:

Pyro-soda without bromide	1.5
Pyro-soda with bromide	1.9
Rodinal, azol, certinal, etc.	1.9
Glycin	2.3
Rytol	2.2
Pyro-soda (Watkins thermo formula), no bromide	1.5
Pyro-soda (Watkins thermo formula), with bromide	1.9
Metol-hydrochinone (Watkins thermo formula)	1.9
Hydrochinon	1.4 –2.25
Ortol	2.06

The use of developing agents of low energy, such as hydroquinone, at low temperatures may result in incomplete development, producing the effect of underexposure.

With a developing solution containing two developing agents one of which is highly sensitive to temperature changes, in other words having a high temperature coefficient and one having a lower temperature coefficient—not only the time but the character of development changes with the temperature. Thus in an elon-hydroquinone developer, only the elon functions actively as a developer at low temperatures, since hydroquinone is active as a developer only at temperatures 60° F. and higher. Elon-hydroquinone developer, therefore, should not be used at a temperature below 55° F.

Developing at a high temperature has a number of practical disadvantages: (1) the tendency of the developing solution to fog is increased; (2) the developing solution oxidizes more rapidly, which increases the tendency to stain and results in more rapid exhaustion of the developer; and (3) the gelatin swells excessively, which leads to blistering, frilling and reticulation of the film.[43]

Calculation of the Time of Development at Different Temperatures.—To construct a table, or graph, showing the time of development at different temperatures, the procedure is as follows:

1. Develop a number of sensitometric strips for different times. Plot the *D* log *E* curves, measure the gammas of the different curves and finally construct a time-gamma curve.

2. Follow the same procedure but with the developing solution at a different temperature, preferably not less than 10 degrees Fahrenheit.

3. Determine from the two time-gamma curves the time of development for the desired gamma at each of the two temperatures.

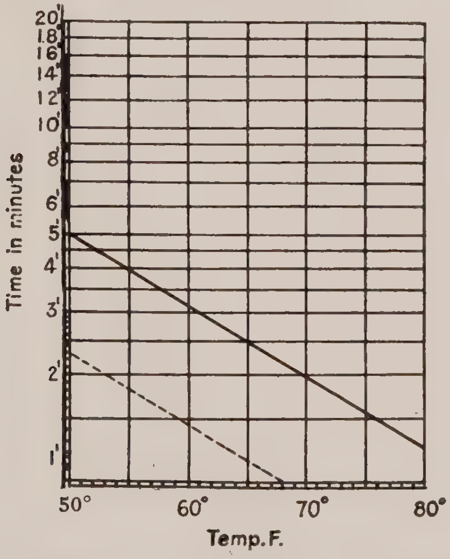

FIG. 209. Showing Method of Constructing a Graph for Representing the Time of Development at Different Temperatures.

4. Plot the two developing times on a chart such as that in Fig. 209 in which temperature is plotted against the time of development, the latter axis being logarithmic. Draw a straight line through the two points as plotted. This line indicates, with sufficient accuracy for practical purposes, the time of development at different temperatures

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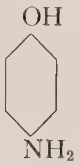
[43] Technique of developing at high temperature. See Page 543.

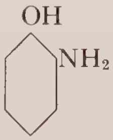
ranging from 50° to 80° F., except that with some low energy developers, such as hydroquinone, the time of development at the lower temperatures may be considerably greater than indicated.

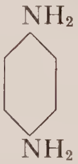
The temperature coefficient for the developer in question may be obtained by dividing the time of development at temperature t by the time of development at temperature $t + 10°$ C. or 18° F.

Coupling Developing Agents.—The known facts regarding coupling developing agents may be summarized as follows:

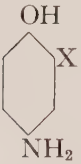
1. Para-amino-phenol, ortho-amino-phenol and paraphenylene-diamine may act as color or *chromogenic* developing agents.

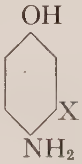


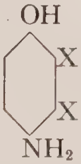


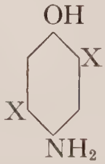


2. Ortho-amino-phenols have reduction potentials which are too low to be practical. The addition of halogen (X) to the molecule increases the reduction potential and renders them suitable for use in color processes. The addition of two halogen atoms increases the reduction potential.

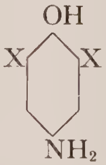




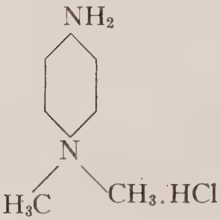




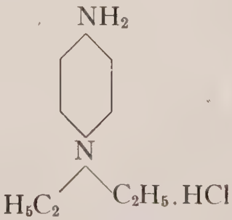
but not



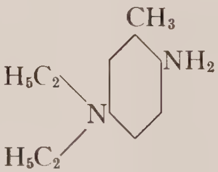
3. In paraphenylene diamine one amino group may be mono or di substituted. The molecule, however, must have one free NH_2 group. The best color developing agents are:



dimethyl-paraphenylene-diamine-hydrochloride

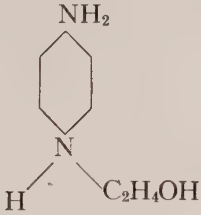


diethyl-paraphenylene-diamine-hydrochloride

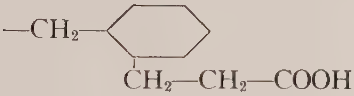


2-amino-5 di-ethyl-amino-toluene

4. The hydrogens in one amino group may be substituted with oxyalkyl groups,



5. Groups containing a carboxyl, sulfonic acid or sulfonamide radical may be substituted for the hydrogen in an amino group. These groups increase the solubility of the compound.

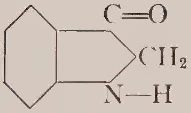


carboxyl

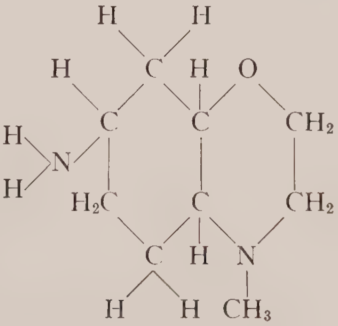
$-CH_2SO_2.NH_2$

sulfonamide

6. The amino nitrogen may be part of a heterocylic ring structure.

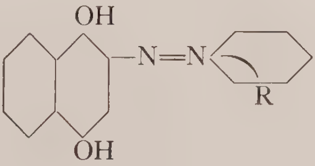


indoxyl

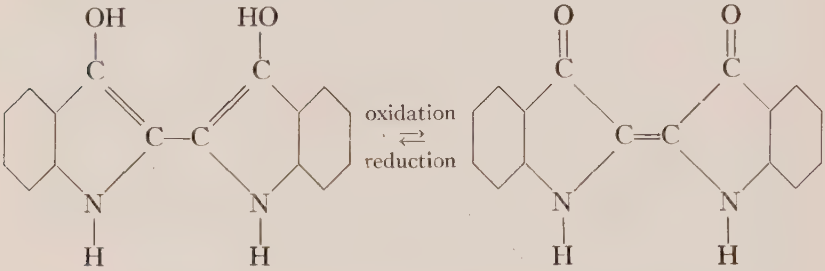


6-amino-N-methyl-penomorpholine

7. Certain compounds retain developing power even when diazonium salt is coupled to the agent, i.e. naphthaquinone.



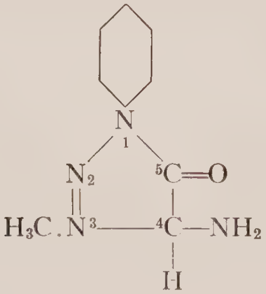
8. Leuco derivatives of certain vat dyes may be prepared in stable forms. These act as developers in alkaline solution, forming colored insoluble oxidation products. In the leuco, reduced form, the dye is colorless and soluble.



indigo white
(soluble)
leuco base

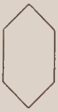
indigo blue
(insoluble)
dye

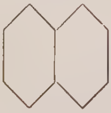
9. Pyrazolone derivatives may act as color developers, i.e. 1-phenyl-3 methyl-4 amino-5 pyrazolone.



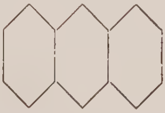
Coupler Characteristics.—The known facts regarding coupler characteristics may be summarized as follows:

1. The coupler should be a member of the aromatic group as:

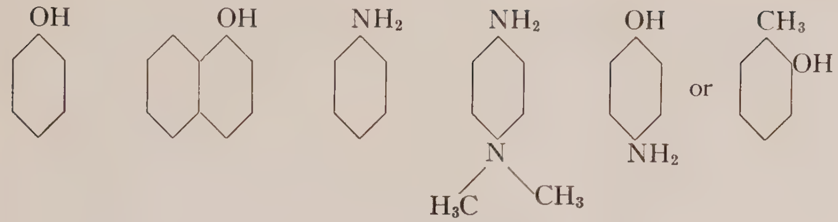

benzene


naphthalene

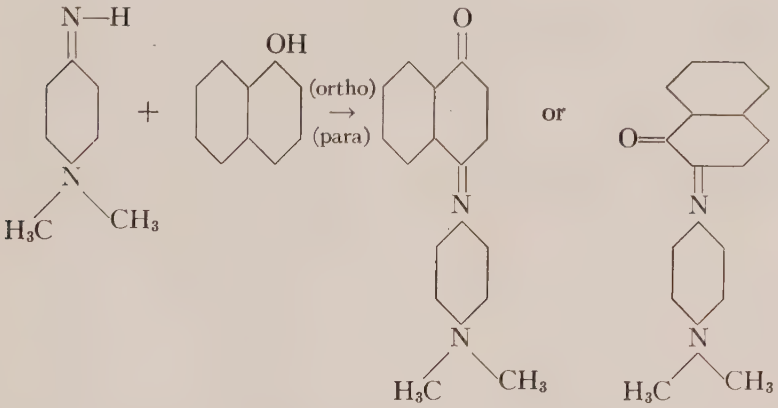
or


anthracene

2. The coupler should contain an OH or NH_2 group in the molecule:



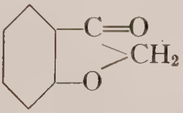
3. Coupling takes place with the hydrogen atom in the ortho or para position to the OH or NH_2 group of the coupler.

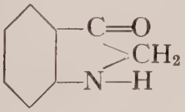


4. Active hydrogen can be replaced by quinoneimides or diazonium groups.

5. Compounds having an active methine CH_2 group, with strong polar groups for other valences, will couple. Suitable polar groups are: the cyano group, —CN; the carbonyl group, =CO; also aceto, CH_3CO—, the acid ester group as —$COOC_2H_5$, and C_6H_5, but not the C_2H_5 group.[44]

6. The methine group may be part of a ring, as in Coumarone and Indoxyl.[45]





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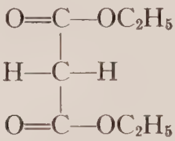
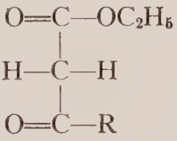
[44] Friedman, *Amer. Phot.* 34 (1940) 452

[45] Friedman, *Amer. Phot.* 34 (1940) 918.

7. The methine group may be a part of a non cyclic structure, as malonic esters and their derivatives:



$$\begin{array}{c} O{=}C{-}OC_2H_5 \\ | \\ H{-}C{-}H \\ | \\ O{=}C{-}OC_2H_5 \end{array}$$



$$\begin{array}{c} O{=}C{-}OC_2H_5 \\ | \\ H{-}C{-}H \\ | \\ O{=}C{-}R \end{array}$$

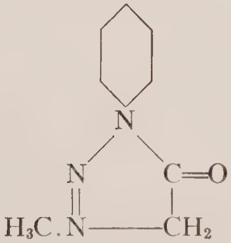
and aceto acetic esters:

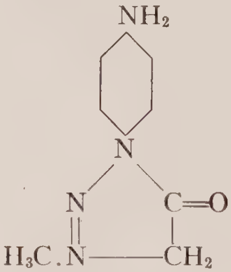
$$CH_3COCH_2COOC_2H_5$$

or a part of a side chain attached to a phenyl group as para nitrophenyl acetonitrile:

$$O_2N.C_6H_4.CH_2CN$$

8. The methine group may be a part of a heterocyclic ring attached to a phenyl group, as 1-phenyl-3 methyl-5 pyrazolone.

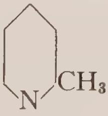




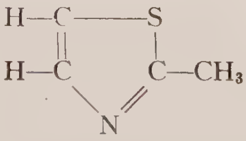
(exception)

An exception to the above is that when a free amino group, NH_2, is attached to the para position of the phenyl group, coupling takes place at the amino group first.

9. Compounds having a N in ring will couple if there is a CH_3 group in the alpha position to the N, as



picoline



2-methyl-thiazole

10. Various derivatives of acetamide and acetoacetamide may act as couplers:

$$\mathrm{X\text{—}CH_2C{=}O\text{—}N{=}}y \qquad \mathrm{CH_3C{=}O.CH_2C{=}O\text{—}NH\text{—}}y$$

where $\mathrm{X} =$ a polar group and $y =$ a heterocyclic base containing nitrogen.

Chemical Constitution and Dye Color.—Practically all organic compounds absorb some light in the ultra-violet. Unsaturated compounds absorb light of longer wave lengths than saturated compounds. See Table below. When a portion of the visible light is absorbed the compounds appear colored.

Dyes are colored organic compounds which are capable of dyeing a fiber or surface without the use of a mordant. The dye molecule is composed of an aromatic or heterocyclic nucleus to which are attached *chromophore* groups, responsible for color; and *auxochrome* groups, responsible for fastening dye to the fiber. The color of a dye may be deepened by adding groups which increase the molecular weight.

REGION OF ADSORPTION SPECTRA FOR SOME UNSATURATED GROUPS

Group	Wave Length	Region	
Ethylene derivatives	200 $\mathrm{m}\mu$	Ultra Violet	
Dienes			
Aromatic compounds			
Carbonyls	300 $\mathrm{m}\mu$		
Acroleins			Visible
	400 $\mathrm{m}\mu$	Violet	
Glyoxals			
		Blue	
Quinones	500 $\mathrm{m}\mu$	Green	
		Yellow	
Crystal violet	600 $\mathrm{m}\mu$	Orange	
Indophenol			
	700 $\mathrm{m}\mu$	Red	
	800 $\mathrm{m}\mu$		

Groups which intensify or deepen the color are known as *bathochromic* groups while groups which diminish color are known as *hypsochromic* groups. According to the Witt dye terminology, a colored substance containing *chromophore* groups is a *chromogen.* A *dye* results when auxochrome groups are added to the chromogen.

Important chromophore groups include:

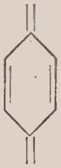
$-N{=}N$
Azo

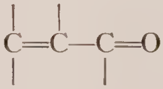
$-NO_2$
Nitro

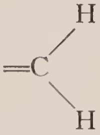
$-N{=}O$
Nitroso

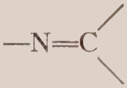
$=C{=}O$
Carbonyl

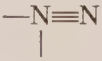
$-C{\equiv}N$
Cyano


Para quinoid


$$>C{=}C<\!-\!C{=}O$$
Unsaturated Ketone


Methine


Azo Methine


$$-\overset{}{\underset{|}{N}}{\equiv}N$$
Diazonium

$-NH.CO-$
Carboxyl amide

$-SO_2.N{=}$
Sulfonamido

$-CO-CH_2-CO-$
Acetoyl-acetyl

Important auxochrome groups include:

$-OH$
Hydroxy

$-NH_2$
Amino

$-N(CH_3)_2$
Dimethylamino

$-OCH_3$
Methoxy

$-SO_3H$
Sulfonic

$-COOH$
Carboxyl

The presence of $-NH_2$, $-OH$, $-N(CH_3)_2$ and $-OCH_3$ in aromatic nucleus deepens color, exerts bathochromic effects; while the presence of SO_3H and $COOH$ groups diminish color, show hypsochromic effects.

In dye coupling, color changes are observed when the hydrogens in either the developing agent or the coupler are replaced with groups that increase the molecular weight.

The effect of adding methyl and ethyl groups to a developing agent which is coupled with di-chlor-alpha-naphthol will serve as an illustration.

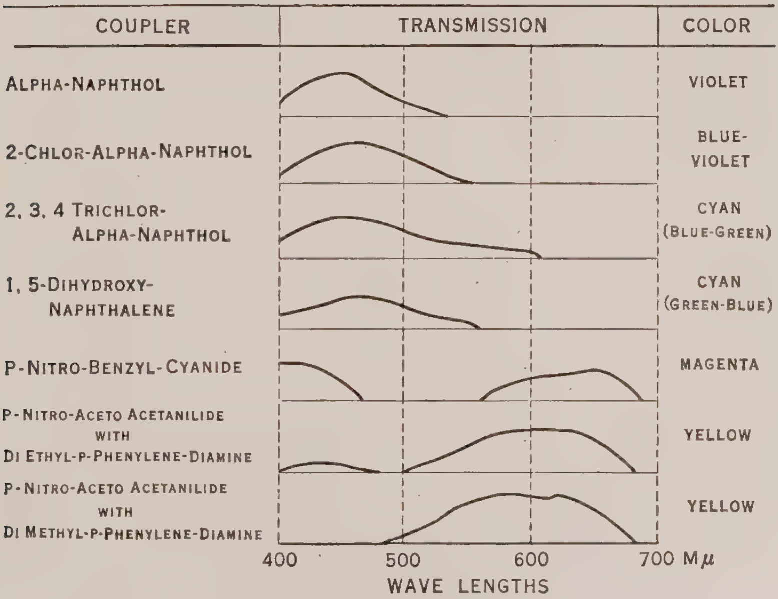
DICHLORO ALPHA NAPHTHOL (COUPLER)

Developing Agent	Group Added	Color
Para-phenylene-diamine		Pink or purple
Para-toluene-diamine	CH_3 on ring	Blue
Di-methyl-para-phenylene-diamine	Two CH_3 groups on N	Cyan
Di-ethyl-para-phenylene-diamine	Two C_2H_5 groups on N	Deeper cyan

A similar effect is observed when substitutions are made in couplers of the hydroxy benzene type, which are coupled with di-ethyl-para-phenylene-diamine, as the developing agent.

DI-ETHYL-PARA-PHENYLENE-DIAMINE (DEVELOPING AGENT)

Coupler	Group Added	Color
Phenol		Greenish blue
O- or P-cresol	CH_3	Cyan
1-3-5-Xylenenol	Two CH_3	Green cyan
Alpha-naphthol		Blue
Di-chlor-alpha-naphthol	Two Cl	Cyan
Tri-chlor-alpha-naphthol	Three Cl	Green cyan
Penta-chlor-alpha-naphthol	Five Cl	Green



Methine couplers give another series of colors.[46]

Coupler	Color
Aceto-acetic-ester	Yellow
Benzoyl-acetic-ester	Reddish yellow
Di-benzoyl-methane	Redder yellow
Cyan-aceto-acetic-ester	Orange
Phenyl-cyan-methyl-acetone	Red

Tull[47] made a survey of dye-coupling methods and has listed the color of images in accordance with the type of compound used. For primary development typical compounds giving colored images are:

Red	Blue	Yellow
Thioindoxyl	Indoxyl	2,5-Di-aryl-hydroquinone
1-Phenyl-amino-beta-naphthol		2,5-Di-phenoxy-hydroquinone
3-Phenyl-amino-alpha-naphthol		Ortho-amino-meta xylenol
		Ortho-amino-phenol
		6-amino-ortho-cresol

In general, dyes of this class include: substituted hydroquinones, acylamino derivatives of hydroquinone or di-oxynaphtholamines, generators of lignon dyes, and ortho-amino-phenols.

Couplers for secondary development were classified according to color produced with ortho or para-aminophenols, phenylenediamines and their substituted derivatives. Typical compound classes are:

Magenta	*Cyan*	*Yellow*
Nitriles	Phenols	Substituted ketones
Acyl nitriles	Naphthols	Certain esters
Thioindoxyls	Indoxyls	Acetoacetic esters
Cyanacetanilides		Chlor acetoacetic esters
Pyrazolones		Cyan acetoacetic ester
		Acyl acetanilides
Derivatives of:	Derivatives of:	Derivatives of:
Lignones	Hydroxy quinolones	Alpha naphthols
Coumarones	Thiazolones	Nitro-bensyl-cyanides
Fluorenes	Thiazalidones	Pyrozolones
Hydrazolones	Benzimidazoles	Isoquinolones
Oxazolones		
Oxindoles		

If one attempts to generalize further, it is interesting to note that in color photography most cyan dyes are formed with a hydroxy benzene, or naphthalene, etc. coupler. Yellow dyes are formed with various derivatives containing the $—CO—CH_2—CO—$, acetoyl-acetyl group.

[46] Friedman, *Amer. Phot.* **34** (1940) 918.

[47] Tull, *Brit. J. Phot.* **86** (1938) 647.

Magenta dyes are often pyrazolone or aceto-nitrile derivatives. Both the yellow and the magenta dyes may be considered to be formed with couplers containing the active methine group, $=CH_2$.[48]

Developing agents for color development satisfactory for amateur use are:[49]

Diethyl-paraphenylenediamine hydrochloride
2-Amino-5-diethylaminotoluene hydrochloride
Dimethyl-para phenylenediamine hydrochloride

Couplers suitable for monochrome and tricolor work include:

Cyan: 2, 4-Dichloro-1-naphthol
  2, 3, 4-Trichloro-1-naphthol
Yellow: Ethyl-acetoacetate
  Acetoacet 2, 5-Dichloroanilide
Magenta: Para-nitrophenyl acetonitrile
  1-Phenyl-3 methyl-5 pyrazolone

Processing formulas for the dye coupling of prints have been given by Wilson, Colton and Möen.[50]

Difficulties.—Dye coupling processes present many problems. It is difficult to obtain developing agents that are sufficiently soluble and are not toxic. To be desired, are couplers that do not require the use of organic solvents, but will produce dyes of the right color shade and yet remain insoluble, so as not to diffuse or bleed. The reagents used should not produce a color fog. The dyes formed should be resistant to processing solutions and reasonably stable to acids, light, heat and humidity.

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[48] Friedman, *Amer. Phot.* 34 (1940) 456. Saunders-Dolgoruki, *Photo. Tech.* 3 (1941) 63.

[49] Chemicals for color development may be obtained from the Organic Chemicals Division of the Eastman Kodak Company.

[50] Wilson, *Amer. Phot.* 33 (1939) 161. Colton, *Phot. Tech.* 1 (1939) Sept., p. 16. Möen, *Phot. Tech.* 3 (1941) June, p. 64.

CHAPTER XI

FIXING, WASHING AND DRYING

The Chemistry of Fixation.—The removal of the silver halide remaining in the emulsion after development is termed fixing. Only a few substances are capable of converting the silver halides into soluble compounds and of these sodium thiosulfate ($Na_2S_2O_3.5H_2O$), commonly termed hypo and sometimes incorrectly referred to as sodium hyposulfite, is the only one of practical utility.[1]

The precise chemical reactions involved in the fixing process are still obscure.[2] Thiosulfate ions undoubtedly combine with silver ions to form various soluble complex ions, as for example

$$
\begin{aligned}
&AgBr + 3Na_2S_2O_3 \rightarrow NaBr + Na_5Ag(S_2O_3)_3,\\
&AgBr + 2Na_2S_2O_3 \rightarrow NaBr + Na_3Ag(S_2O_3)_2,\\
&2NaBr + 3Na_2S_2O_3 \rightarrow 2NaBr + Na_4Ag_2(S_2O_3)_3.
\end{aligned}
$$

A number of such complexes are possible and in a used fixing bath it is probable that several are present in equilibrium, the particular ones present depending upon the relative concentrations of thiosulfate and silver. It is possible that in a fixing bath containing only a small amount of silver the complexes may contain even more thiosulfate than those in the equations, while in a used fixing bath the slightly soluble $NaAgS_2O_3$ may be found.

Since these insoluble, or slightly soluble, complexes are unstable, they will, if left in the film, decompose in time, producing a silver sulfide stain.

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[1] The sulphocyanides as fixing agents. Cf. Piper, *Brit. J. Phot.* **61** (1914) 458, 511.

[2] Herschel, *Edinburgh Phil. J.* **1** (1819) 8, 396. Baines, *Phot. J.* **69** (1929) 314. Sheppard, Elliott and Sweet, *J. Franklin Inst.* **195** (1923) 45.

BAINES—Chemistry of Fixation. Phot. J. **69** (1929) 314–317.
RENWICK—Principles and Practice of Fixation. Phot. J. **69** (1929) 310–314.
SHAW—Fixation and Permanence. Brit. J. Phot. **80** (1933) 214.
SHEPPARD AND MEES—Theory of Fixation. Phot. J. **46** (1906) 235.
WARWICK—The Laws of Fixation. Amer. Phot. **11** (1917) 585.

Acid Fixing Baths.—While a solution of hypo will dissolve silver halide, it does not form a satisfactory fixing bath because the developing solution on the surface of the films or prints, when placed in the fixing bath, oxidizes and causes stain. Staining may be prevented, however, if a substance, such as sodium sulfite, which tends to prevent the oxidation of the developer, is added to the fixing bath. The addition of a weak acid neutralizes the alkali introduced by the developer, maintains the bath in an acid condition, and assists the sodium sulfite in preventing the oxidation of the developing agent thus greatly increasing the period over which the fixing bath may be used without danger of staining.

The most convenient method of preparing an acid fixing bath is by the use of an acid sulfite such as sodium bisulfite ($NaHSO_3$).

Hypo	250 gm.	8 oz.
Sodium sulfite	10 gm.	145 gr.
Sodium bisulfite	25 gm.	365 gr.
Water to make	1000 cc.	32 oz.

The sodium sulfite is added to prevent possible precipitation in hot weather.

With use, the reserve acidity is soon neutralized by the developer brought over into the fixing bath and it becomes necessary either to discard the bath or to add a 25% solution of sodium bisulfite in sufficient quantity to render the bath acid.

Acid fixing baths of this type are satisfactory when it is not necessary to harden the gelatin or if a hardening stop bath is employed after developing and prior to fixing.

Acid Fixing and Hardening Baths.—A combined acid fixing and hardening bath contains the following ingredients: (1) a solvent of silver halide, (2) an anti-staining agent, (3) a preservative, and (4) a hardening agent.

These ingredients ordinarily are hypo; an organic acid, usually acetic; sodium sulfite and alum.

It is the function of the acid to neutralize the alkali in the developer carried over on the film preventing oxidation thus keeping the bath clear and free from staining tendencies. The addition of acid to a solution of hypo decomposes the hypo forming sulfur and sulfurous acid, and destroys the fixing power of the bath. To prevent the precipitation of sulfur, sodium sulfite, which combines with sulfur to form hypo, is added. An acid fixing bath is thus rendered stable by the sulfite, which also assists in preventing the oxidation of the developing solution carried over into the fixing bath.

Organic acids, such as acetic, citric and oxalic, are better adapted to these requirements than inorganic acids, such as sulfuric or hydrochloric, because being less disassociated they do not tend to precipitate sulfur from a solution of hypo so readily. Solid organic acids, on the other hand, produce with aluminum salts (such as the alums) complex aluminum ions which are not satisfactory as hardening agents. The acid sulfites, such as sodium bisulfite and potassium metabisulfite, are not suitable for a fixing bath containing alum, as the reserve acidity is not sufficient to prevent the precipitation of aluminum sulfite upon the addition of alkali.

Hardening of the gelatin may be produced by salts of aluminum, chromium, and iron, by formaldehyde, tannin, and by quinones and quinonid bodies. Of these only the alums and formaldehyde are suitable for use in fixing baths. The hardening produced with alum is due to the hydrolytic separation of the alum into hydrous oxide and free acid,

$$Al_2(SO_4)_3 + 3H_2O \leftrightarrows Al_2O_3 + 3H_2SO_4.$$

The alumina, or other oxide, combines with the gelatin probably as an absorption complex and is retained on washing in hot water.

Crabtree and Russell—Some Properties of Chrome Alum Stop Baths and Fixing Baths: I. Chrome Alum Stop Baths. II. Chrome Alum Fixing Baths. J. Soc. Mot. Pict. Eng. **15** (1930) 483–512, 667–700.

Crabtree and Russell—Acid Hardening Fixing Composition. (Eastman Kodak Co.) U.S.P. 2,063,297 of 25.10.34.

Elliott, Sheppard and Sweet—The Chemistry of the Acid Fixing Bath. J. Franklin Inst. **196** (1923) 45.

Kieser—Chemistry of Fixing Baths. Phot. Ind. **32** (1934) 696; Sci. et Ind. Phot. (II) **5** (1934) 252.

Luther and Rommler—Chemistry of the Fixing Bath. Phot. Ind. (1928) 626.

Muehler—Liquid Hardener Solutions. (Eastman Kodak Co.) U.S.P. 1,981,426 of 18.4.33.

Russell—Acid Hardening Fixing Bath. (Eastman Kodak Co.) U.S.P. 1,981,391 of 27.9.32.

Russell and Crabtree—An Improved Potassium Alum Fixing Bath Containing Boric Acid. J. Soc. Mot. Pict. Eng. **21** (1933) 137.

Staud and Briggs—Hardening Photographic Gelatin Emulsions and Gelatin Solutions. Kodak Ltd. B.P. 444,289 of 4.8.34.

Sheppard—Hardening Photographic Gelatin Emulsion and Solutions. (Eastman Kodak Co.) U.S.P. 2,059,817 of 27.9.34.

The hardening action of formaldehyde is due probably to the interaction of the amino groups of the gelatin with formaldehyde resulting in the formation of an insoluble compound of undetermined composition.[3]

Chrome Alum Fixing Baths.—A properly compounded chrome alum fixing bath hardens gelatin more completely than one of potassium alum, but its hardening properties fall off more rapidly, unless acid is added from time to time to maintain the proper acidity. Chrome alum fixing baths are desirable when processing at high temperature, if the wash water is warm, or if it is necessary to dry rapidly at high temperature. Except under such conditions, potassium alum baths are usually more satisfactory owing (1) to their longer life and (2) because chrome alum baths when partially exhausted may harden the surface of the gelatin and not the underlying layers, which would tend to cause reticulation.

Preparation of Fixing Solutions.—No difficulty is usually experienced when mixing a plain hypo solution. When mixing a quantity of solution in a tank, the filter bag should be used and the hypo dissolved in warm water, because the temperature drops considerably while the hypo is dissolving. If a scum forms on the surface of the solution on standing, it should be removed by drawing the edge of a towel or blotter, or a cheesecloth skimmer, across the surface.

In preparing an acid fixing bath which contains either sodium bisulfite, or potassium metabisulfite, care should be taken not to add these to the warm hypo solution; otherwise sulfur will be precipitated and the bath rendered milky. The solution should be quite cold (not above 70° F. (21° C.)) when mixed.

In preparing an acid fixing and hardening bath, the order of mixing the acid hardener is important. When mixing in one vessel, first dissolve the sulfite in warm water (125° F. (52° C.)); then add the acid; and, finally, the potassium alum. Another method is to dissolve the alum and sulfite in separate solutions, cool, add the acid to the sulfite solution, and then add the alum solution.[4]

The hypo should be cool and completely dissolved before adding the hardener, or sulfur is likely to be precipitated.

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[3] Sheppard, *Photography as a Scientific Implement,* p. 138.

[4] To make 28% acetic acid from glacial acetic acid, dilute three parts of glacial acid with eight parts of water.

In the case of formulas requiring boric acid, the crystalline form should be used. Powdered boric acid dissolves only with great difficulty, and its use should be avoided.

Fixing baths containing chrome alum as the hardening agent generally have sulfuric acid as the active acid. Usually, no difficulty is experienced in preparing such baths, provided care is taken in adding the sulfuric acid to the chrome alum solution. The acid should be added slowly, while the solution is vigorously stirred, in order to insure thorough mixing, since the acid is heavy and will sink to the bottom if not well mixed. Water should never be added to sulfuric acid or the solution may boil and spatter acid on the hands or face, causing serious burns.

The Hardening of Gelatin in Fixing Baths.—The degree of hardening produced in an acid fixing and hardening bath depends upon:

1. *The composition of the bath.* Under given conditions, the degree of hardening produced in an acid fixing and hardening bath employing potassium alum depends upon the pH value of the bath, which in turn is determined by the relative proportions of acid, sulfite, and alum. For each concentration of acid, there is a definite quantity of sulfite, which produces the maximum hardening with a given quantity of alum. An increase in the amount of alum results in a higher degree of hardening, but increases the tendency of the bath to sludge upon the addition of developer.[5]

2. *The time of fixing.* The degree of hardening increases with the time of fixing up to a maximum which depends upon the bath and the conditions of fixing. The time required for maximum hardening may vary from 3 to 15 minutes, depending upon the fixing bath and the thickness of the gelatin layer.

3. *The alkalinity of the film when placed in the fixing bath.* The quantity of alkali in the film when it is placed in the fixing bath is one of the major factors in the degree of hardening produced in an acid fixing and hardening bath. Film which is strongly alkaline is not as thoroughly hardened as that which has been well washed before fixing. For maximum hardening, therefore, film should be well washed after development, or placed in a stop bath, before being transferred to the fixing bath.

4. *The temperature of the fixing and hardening bath.* The degree of hardening increases slightly with the temperature of the fixing bath, but if the temperature of the developer and rinse water, or stop bath, has increased at the same time, the film will not be as thoroughly

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[5] Crabtree and Hartt, *Trans. Soc. Mot. Pict. Eng.* **13** (1929) 364.

hardened because of the increased swelling of the gelatin when placed in the fixing bath. The temperature of the fixing bath and other processing solutions should be maintained between 65° and 70° F. (18° to 20° C.) for maximum hardening.

Effect of Use on a Fixing Bath.—The major changes taking place in a fixing bath as it is exhausted through use are as follows:

1. *The concentration of hypo is reduced.* This reduces the amount available for fixing and tends more and more to form complex ions of silver thiosulfate which are either slightly soluble, or insoluble, in water.
2. *Sodium silver thiosulfate, sodium bromide (and iodide in the case of sensitive materials containing iodide) accumulate in the bath.* The exact formula of the silver compound is not definitely known but is probably $Na_4Ag_2(S_2O_3)_3$.[6]

The fixing properties of the bath are not materially affected by the silver compound—except to the extent to which it represents a reduction of the original hypo concentration—but the accumulation of alkaline halide, particularly potassium iodide, greatly retards the rate of fixing and materially reduces the fixing properties of the bath.[7] The presence of even a small amount of iodide is sufficient to prevent thorough fixation, although the amount of silver present in the fixing bath is far below the saturation point.

3. *The hardening properties are reduced as a result of the gradual neutralization of the free acid in the fixing bath by the alkali carried over on the film.* When the acidity of the bath has been reduced beyond a certain value, usually near the neutral point, a sludge of aluminum sulfite forms and the hardening properties are destroyed. The amount of alum adsorbed, or otherwise removed from the bath in hardening, is negligible and is without practical effect on the hardening properties of the bath.[8]

The limits to which a fixing bath may be used, with the assurance of thorough fixation, depends on (1) its ability to convert the silver halides into soluble silver sodium thiosulfate compounds and (2) its ability to harden the gelatin sufficiently.

When sensitive materials containing silver iodide are fixed, the saturation point of solutions of hypo is fixed by the amount of silver iodide present. The presence of silver iodide above the saturation point prevents complete fixation, even if the amount of dissolved silver is much below the saturation point.[9]

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[6] Barth, *Z. Phys. Chem.* **9** (1912) 218.

[7] Busch and Lehrmann, *Brit. J. Phot.* **75** (1927) 91.

[8] Crabtree and Hartt, *Trans. Soc. Mot. Pict. Eng.* **18** (1929) 364.

The investigations of Busch and Lehrmann indicate that in a solution of hypo containing 150 gm. to 1000 cc. the bath is exhausted when the silver content reaches 0.6–0.7%. If a negative emulsion is assumed to contain 0.10 gram silver per square meter, then for practical purposes each ounce of fixing bath should be sufficient for approximately 15 square inches of plate or film.

In practice, the time of clearance—which is a direct indication of the time required for fixing—is so greatly increased by the restraining effect of the accumulated alkaline halides that the bath is discarded before the limit is reached because of the time required to clear. As a general rule, a fixing bath should be discarded when the time of clearing is double that of a fresh solution, assuming in each case the same sensitive material.

With a potassium alum fixing bath containing boric acid, the hardening properties under normal conditions are not substantially reduced before the bath is exhausted. With potassium alum fixing baths which do not contain boric acid, and more particularly with chrome alum fixing baths the loss of hardening properties usually makes it necessary to discard the bath before it is exhausted, unless the acidity is maintained by the addition of acid from time to time.

The Testing of Used Fixing Baths.—The amount of silver present in a used fixing bath may be determined by adding a solution of sodium sulfide to a sample of the bath diluted with water. A brown precipitate is produced, the depth of which depends upon the amount of silver. The quantity of silver present may be determined by comparing the color of the test solution—held before an illuminated screen in a glass tube—with other tubes containing a known concentration of silver sulfide.

There are two drawbacks to this method of testing a fixing bath:

(1) the standardized comparison solutions do not keep well; (2) the color of the precipitate from a fixing bath varies with the acidity, the sulfide, and alum content of the bath, as well as the quantity of silver present.

[9] Busch and Lehrmann, loc. cit.

LEHRMANN AND BUSCH—Fixing Baths and their Better Utilization. Kinotechnik Jahrbuch, 1925/26, 114–130; Sci. et Ind. Phot. **6** (1926) 148.

The last-mentioned drawback may be overcome by using the following test solutions:

Solution A

Citric acid	9 gm.	1¼ oz.
Sodium citrate	100 gm.	13 oz.
Water to make	1000 cc.	128 oz.

Solution B

Gelatine	4 gm.	½ cz.
Water to	1000 cc.	128 oz.
Clove oil (a few drops for preservation)		

Soak the gelatin in a small amount of water until well swollen, then heat gently, stirring until all is in solution; dilute to proper volume with water and pour into a bottle; add the clove oil and shake a few times.

Solution C

Sodium sulfide (CP Crystals)	10 gm.	1 oz.
Sodium sulfite (desiccated)	6 gm.	260 gr.
Water to	100 cc.	10 oz.

A sample of the fixing bath is measured out with a 2 cc. pipette and allowed to drain into a 50 cc. graduated cylinder. Five cubic centimeters of solution *A* are added, and then 5 cc. of solution *B* after which the cylinder is filled to the 50 cc. mark with water. Add 1 cc. of solution *C* and compare the opacity of the resulting precipitate with a standardized solution containing a known quantity of silver.

The concentration of silver in a sample of the fixing bath to which the testing solution has been added may be found by measuring the opacity of the precipitate. An instrument known as the Argentometer, employing a photronic cell, has been introduced by the Eastman Kodak Company for making such measurements quickly and conveniently.[10]

The following method based upon the formation of a precipitate of silver iodide has also been recommended for determining when a fixing bath is exhausted:

Withdraw 10 ounces (100 cc.) of the fixing bath and add 1 ounce (10 cc.) of a 4% solution of potassium iodide. The bath may be regarded as exhausted if a yellow precipitate is formed on standing.

Another method suggested frequently is as follows: immerse a strip of film, or bromide paper, in the fixing bath until clear, then wash for several minutes and place in a 1% solution of sodium sulfide. The appearance of a brown discoloration indicates the presence of silver halide due to imperfect fixation.

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[10] "The Argentometer—An Apparatus for Testing for Silver in a Fixing Bath," W. J. Weyerts and K. C. D. Hickman. *Brit. J. Phot.* **82** (1935) 739.

The Time of Fixing.—The time required for the conversion of the silver halide into soluble complexes of sodium silver thiosulfate depends upon a number of factors:

1. *The nature and the thickness of the emulsion.* In general, fine-grain emulsions, such as those employed for positive printing, fix much more rapidly than negative emulsions which are composed of larger grains. Emulsions containing silver iodide fix more slowly than those of silver bromide, and these in turn more slowly than emulsions of silver chloride. A thickly coated material requires a longer time to fix than a thin one, if both emulsions are of the same general character.

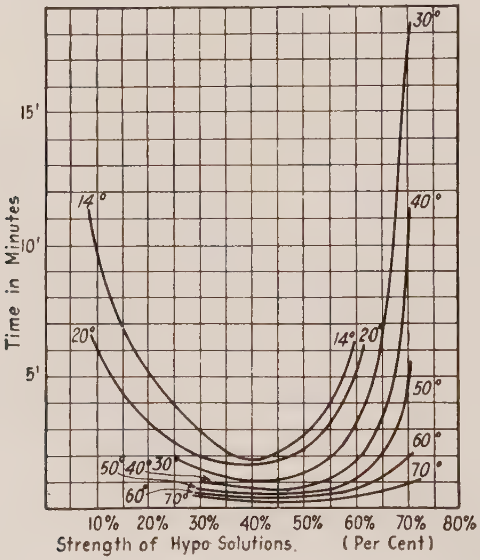

FIG. 210. Rate of Fixing at Various Hypo Concentrations.

2. *The nature and degree of exhaustion of the fixing bath.* The rate of fixing varies with the concentration of hypo, generally increasing up to a concentration of 30 to 40%, and then decreasing (Fig. 210). The concentration at which the maximum rate of fixing is obtained depends in part upon the nature of the emulsion.

The addition of ammonium chloride to a plain hypo solution (not above 70° F.) increases the rate of fixing, but fixing baths of this type may not be so thoroughly exhausted as an acid fixing and hardening bath.[11] The effect varies with the amount of ammonium chloride added and the concentration of the hypo solution (Fig. 211).

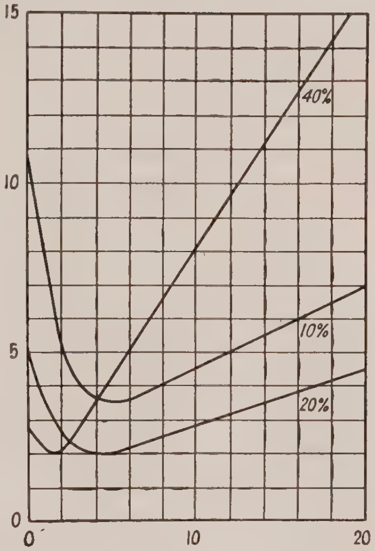

FIG. 211. Effect of the Addition of Ammonium Chloride to the Fixing Bath on the Time of Fixing. The Time of Fixing is Plotted on the Vertical Axis Against the Amount of Ammonium Chloride in Grams per Liter for 10, 20, and 40% Solutions of Hypo. (Piper.)

The time required for fixing increases as the solution becomes exhausted owing (1) to the lower concentration of hypo and (2) to the restraining effect of the alkaline halides which accumulate in the bath.[12]

3. *The temperature of the fixing bath.* The effect of temperature varies with the concentration of hypo (Fig. 212). At temperatures above 70° F. (21° C.) an acid fixing and hardening bath tends to sulfurize, and the degree of hardening is reduced, as the gelatin swells excessively before the hardening action becomes effective.

4. *The degree of agitation.* Agitation reduces the time required in fixing, but the effect is much less with fine-grain positive materials than with negative emulsions of coarser grain and more thickly coated.

Silver Recovery.—There are several methods by which the silver in a used fixing bath may be recovered; usually, however, the

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[11] Lumière and Seyewetz, *Bull. Soc. franç. Phot.* (1908) 217. Piper, *Brit. J. Phot.* **61** (1914) 193, 437, 458, 511; **62** (1915) 364. Agfa, B.P. 25,869 of 1906.

[12] Strauss, *Phot. Ind.* **23** (1925) 911. Crabtree and Ross, *Amer. Annual of Phot.* (1927) 159.

LUMIÈRE AND SEYEWETZ—The Time of Fixing of Developing Papers. Brit. J. Phot. **71** (1924) 108; Bull. Soc. franç. Phot. (1924) p. 31.

LUMIÈRE AND SEYEWETZ—The Fixing of Photographic Negatives. Rev. franç. Phot. **5** (1924) 61.

PIPER—The Rate of Fixing. Brit. J. Phot. **60** (1913) 59.

WARWICK—The Fixation of Prints. Amer. Phot. **11** (1917) 639.

financial return is hardly sufficient to justify the expense and labor involved, except when dealing with large volumes of fixing bath.[13]

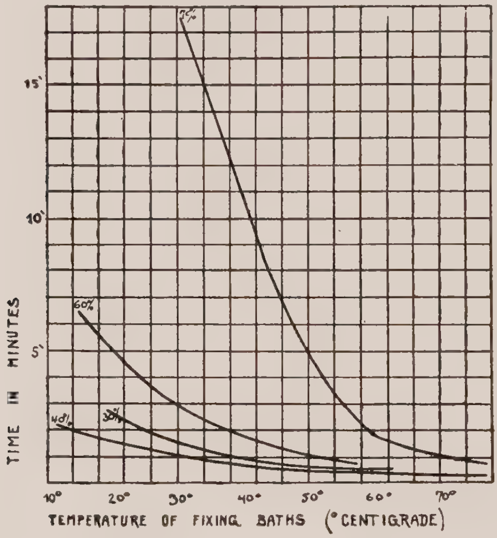

FIG. 212. Curves Showing the Effect of Temperature on Time of Fixing.

Silver Recovery with Sodium Sulfide. This is one of the most satisfactory methods of precipitating the silver in a used fixing bath as it is rapid and economical, but acid fixing baths must first be neutralized with caustic soda to prevent unpleasant fumes of hydrogen sulfide.

The chemistry of the reaction is as follows:

$$Na_2S + Na_4Ag_2(S_2O_3)_3 = Ag_2S + Na_2S_2O_3.$$

Proceed as follows: Prepare a solution of caustic soda by dissolving 2 lb. of commercial caustic soda in one gallon of cold water (240 grams in 1000 cc.).

Add one ounce of the solution of caustic soda to each gallon of the used fixing bath, stir well and test with *red* litmus paper. If the litmus paper does not turn blue, add more caustic soda until it does. Finally, add 1/5 oz. of caustic soda per gallon of fixing bath to assure reserve alkalinity.

The solution of sodium sulfide is prepared by dissolving two lbs. in one gallon of water (240 grams to 1000 cc.). The solution should not be prepared in close proximity to sensitized materials.

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[13] Bibliography on processes of silver recovery and resume of methods. Crabtree and Ross, *American Annual of Photography,* 41 (1927) 159.

Add one ounce of this solution to each gallon of the neutralized fixing bath (7.5 cc. to 1000 cc.). Stir well and allow to stand for a few minutes. To determine if the silver has been completely precipitated, withdraw a small volume of the solution, filter, and add a little of the sodium sulfide solution. If a dark precipitate forms, more of the sodium sulfide solution should be added to the fixing bath until the test gives a clear solution.

Allow 10 to 12 hours for the sludge of silver sulfide to settle out and drain off the clear liquid.

Silver Recovery With Zinc. The reaction taking place when zinc is added to a used hypo bath may be written as follows:

$$Na_4Ag_2(S_2O_3)_3 + Zn = 2Ag + ZnS_2O_3 + 2Na_2S_2O_3.$$

The amount of silver recovered is less than with sulfide and precipitation is not as rapid, but no objectionable odors are produced.

Although silver is precipitated by zinc from either acid or alkaline fixing baths, the best results are obtained if the bath is acid. Most discarded fixing and hardening baths are slightly acid; if tests with litmus paper show a particular bath to be alkaline, glacial acetic acid should be added until the bath is distinctly acid.

Either zinc dust, granulated, or sheet zinc may be used, but the rate of precipitation is very slow with the last two.

Using zinc dust, add ⅔ of an ounce to each gallon of fixing bath (5 grams per liter) while stirring constantly. Continue to stir the bath for 3 or 4 minutes and then allow to stand for 16 to 24 hours. Complete precipitation of the silver may be determined by testing with sodium sulfide.

After draining away the clear solution, the sludge should be removed, filtered if necessary, and dried.[14]

[14] The sulfides of lead, iron and hydrogen and sodium hydrosulfite or sodium formaldehyde-sulfoxylate may be used for the recovery of silver from used fixing baths but are no more efficient and relatively more expensive than sodium sulfide or zinc.

ARENS AND EGGERT—Recovery of Silver from Used Fixing Baths. Phot. Ind. **34** (1936) 1011, 1040; Sci. et Ind. Phot. (II) **7** (1936) 402.

HICKMAN AND HYNDMAN—Automatic Silver Recovery from Hypo. Brit. J. Phot. **74** (1927) 683.

CRABTREE AND ROSS—Recovery of Silver from Exhausted Fixing Baths. Brit. J. Phot. **73** (1926) 522–526.

Electrolytic Methods of Recovery. The silver in a used fixing bath may also be recovered by electrolysis. An electric current passing between electrodes immersed in the fixing bath will cause the silver to separate either as metallic silver or as a suspension of silver sulfide, depending upon the difference in potential. Elaborate machinery for recovering silver from fixing baths has been developed and is used widely in motion picture processing laboratories. The silver is recovered as metallic silver and, as the processes employed may be used to remove silver from a fixing bath while in use, it retains its fixing and hardening properties longer.[15] The factor of expense places such equipment beyond the resources of all but the larger laboratories.

Silver recovery units of separated copper and zinc plates forming an electrolytic couple are available commercially. When placed in a fixing bath containing silver, a current flows through the bath from the zinc to the copper; if the potential is about 0.7 volts, metallic silver is deposited on the copper plate. These units produce a sludge if placed in a fixing bath when in use but from a very convenient means of recovering silver from discarded solutions as they require no particular attention. Large containers are necessary for the used baths, however, as from one to two weeks are required for the maximum recovery.

PART II. WASHING AND DRYING

The removal of the hypo and soluble by-products remaining in the film after fixation is essential to the permanency of the image, for if left in the gelatin they decompose, producing colored stains and causing the image to fade. Ordinarily, the elimination of these by-products is accomplished by simply washing in water. Certain substances known as hypo eliminators are used under certain conditions to reduce the time of washing but offer no real advantage except in the case of prints where the last remaining traces of hypo are not removable by simple washing in water.

Time of Washing.—In general, hypo diffuses from the gelatin exponentially with time.[16] In other words, the quantity of hypo leaving the film at any moment is proportional to the quantity present at the same time.

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[15] Hickman, Sanford and Weyerts, *J. Soc. Mot. Pict. Eng.* **17** (1931) 568; Hickman, *J. Soc. Mot. Pict. Eng.* **17** (1931) 591.

[16] Mees and Sheppard, Investigations on the Theory of the Photographic Process, 1903. Lumière and Seyewetz, *Bull. Soc. franç. Phot.* (1902) 251. Warwick, *Brit. J. Phot.* **64** (1917) 261. Elsden, *Phot. J.* **57** (1917) 90. Hickman and Spencer, *Phot. J.* **62** (1922) 225.

Thus, for example, if for each minute of washing, one half of the hypo present leaves the film the amount originally present will be reduced to one fourth in two minutes, one eighth in three minutes, one sixteenth in four minutes and in twenty minutes the amount remaining will be only 1/1,000,000 of that originally present.

The rate at which the hypo diffuses from the gelatin layer depends upon the difference in the concentration of hypo in the gelatin and in the water in contact with it. The lower the concentration of hypo in the water in contact with the gelatin layer, the more rapid the diffusion of hypo from the gelatin. Thus the more rapidly the water in contact with the film is renewed and replaced with fresh, the less the time of

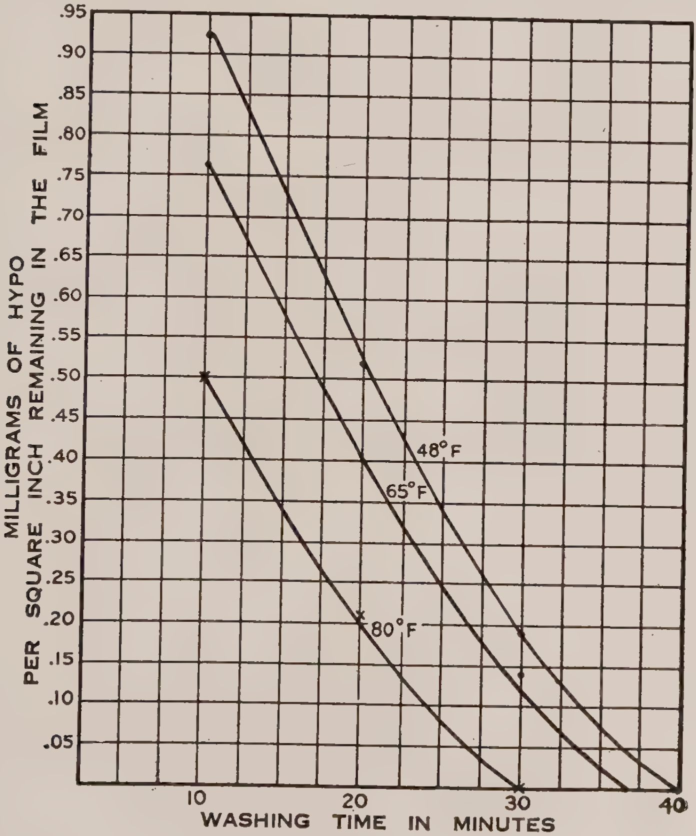

FIG. 213. Curves Showing the Rate of Hypo Elimination from a Negative Material in an "Ideal" Stream.

washing necessary to reduce the amount of hypo by a given amount. The maximum rate of washing is obtained by spray. Experiments have shown that a plate, or film, held directly beneath a tap is washed in from five to six minutes.[17] In a tank, the time of washing depends primarily upon the time required to fill and empty the tank. The more often the water in the tank is changed the shorter the time of washing.

Figure 213 shows the rate of hypo elimination from Verichrome film in an "ideal stream," i.e., one in which a sufficient volume of water passes over the surface of the material so that it removes the hypo from the surface faster than the hypo diffuses out. It will be observed that the rate of hypo elimination increases with the temperature. Crabtree, Eaton and Muehler [18] also found the time of washing to be less for film fixed in a non-hardening fixing bath than in the usual acid fixing and hardening baths.

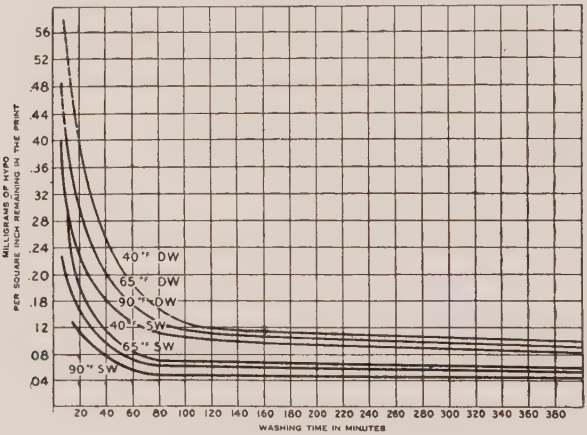

FIG. 214. Curves Showing the Rate of Hypo-Elimination from Papers.

In the case of papers (Fig. 214), the rate of hypo elimination is much more rapid in the early stages of washing than with negative materials, but the last traces of hypo are not removed even upon prolonged washing. This is due apparently to the adsorption of the thiosulfate ion to the fibers of the paper and the baryta coating. It does not appear that papers can be washed sufficiently free of hypo to ensure a high degree of permanency without the use of a "hypo eliminator." See Page 369.

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[17] Hickman and Spencer, *Phot. J.* **62** (1922) 225.

[18] From Crabtree, Eaton and Muehler, *J. Franklin Inst.* **230** (1940) 701.

Since the object in washing is to reduce the hypo in the film to an amount which will ensure the stability of the image, it is evident that, for given conditions of washing, the time depends upon the amount of hypo originally present in the gelatin layer. For this reason, negative film, owing to its thicker coating, requires longer washing than positive materials. Likewise gelatin which is excessively swollen from immersion in warm solutions, or a fixing bath which does not harden, absorbs more hypo and hence requires longer washing than that which has been properly hardened. It is essential, therefore, for rapid washing to prevent the undue swelling of the gelatin (1) by maintaining developing and fixing solutions at the proper temperature, (2) by using a fixing bath which hardens efficiently, and (3) by avoiding developing solutions which because of the time required for development allow the gelatin to swell excessively before it reaches the fixing bath.

Tests for Hypo.—All of the following methods of testing for the presence of hypo may be used with negative materials. The most convenient, but least reliable in practice, is potassium permanganate; the mercuric bromide test is much more sensitive but is slower and samples of the film must be placed in the solution. The iodine azide test is delicate. For prints, the silver nitrate test is the only one possessing a high degree of reliability. The permanganate and iodine-azide methods indicate, with a satisfactory degree of accuracy, the hypo diffusing out from the surface; i.e., the hypo in the wash water—but do not give any indication of the hypo retained in the film or paper. In the case of papers, the water draining from the surface may be practically free from hypo while a considerable quantity—sufficient to cause fading—is still present in the paper base and its baryta coating. For this reason only the silver nitrate test is a reliable indication of the presence of hypo in prints.

Permanganate Test.—When the film is thought to be washed, it is lifted from the washing tray or tank and the surface water allowed to drain into 10 or 20 cc. of the following alkaline potassium permanganate solution:

	Metric	*Avoirdupois*
Potassium permanganate..............	0.5 gm.	7.5 gr.
Sodium hydroxide (caustic soda)........	1.0 gm.	15.0 gr.
Water (distilled) to make.............	1.0 liter	32.0 oz.

For use, take stock solution 1 part, water 20 parts. If a small percentage of hypo is present, the violet color will turn orange in about

30 seconds, and with larger concentrations of hypo the orange color will change to yellow.

Oxidizable organic matter, if present in the water, reacts with the permanganate solution and changes the color in the same manner as hypo. The water, therefore, should be tested as follows:

Add a quantity of water equal in volume to that of the wash water drained from the film to a second test solution prepared as above from pure water. If the sample to which tap water has been added remains a violet color, this indicates the absence of organic matter and it will be unnecessary to repeat the test. If the color is changed slightly by the tap water, the presence of hypo in the film will be shown by the relative color change of the two samples. For example, if the tap water sample turned orange, and wash water sample became yellow, it would indicate the presence of hypo; but if both samples remained the same shade, this would indicate the absence of hypo.

Mercuric Chloride Test.—A more sensitive test consists in placing strips of film in a solution of mercuric chloride, preferably one which also contains potassium bromide, and observing any turbidity which may develop in the solution. If sodium thiosulfate is present, it reacts with the mercuric chloride to form mercurous chloride which is relatively insoluble and causes a turbidity to appear in the solution. If no sodium thiosulfate or other reducing agent is present, the solution remains clear although the silver image is bleached white.

The test solution is prepared as follows:

Mercuric chloride	25 gm.	365 gr.
Potassium bromide	25 gm.	365 gr.
Water to make	1000 cc.	32 oz.

To make the test, place a piece of the washed film about 1 inch square, in a test tube and add about 10 cc. of the test solution. The appearance of a milky precipitate in 10 to 15 minutes is an indication of the presence of hypo.[19]

Lead Azide Test.—A very sensitive test is available in a solution of iodine and starch.

Two stock solutions are made:

A.	Iodide	100 gm.	4 oz.
	Potassium iodide	100 gm.	4 oz.
	Water to	1000 cc.	10 oz.
B.	Sodium azide	100 gm.	4 oz.
	Water to	1000 cc.	10 oz.

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[19] Crabtree and Ross, *J. Soc. Mot. Pict. Eng.* **14** (1930) 419.

A starch mixture is also prepared by mixing 90 grains (6 gm.) of soluble starch with cold water and adding this to 7 oz. (200 cc.) of boiling water. On cooling, dilute to 25 oz. (800 cc.) and add 60 minims of Solution A (3.25 cc.) and 235 minims of Solution B (13 cc.) diluting finally to a total of 35 oz. (1000 cc.). This stock solution keeps well and for use is diluted with 100 parts of water. If a small quantity of this solution is placed in a test tube and the drippings from a negative or print are collected in the tube, the blue color of the solution will be immediately discharged if hypo is present.

Silver Nitrate Test.—This test was suggested by Lumière and Seyewetz [20] in 1908 and again by Weyde.[21] The following directions are due to Crabtree, Eaton and Muehler.[22] Process with the prints an unexposed, white sheet of paper of the same weight and kind as the majority of prints in the batch. To test for hypo, tear off a test strip and immerse a portion of it in a 1% solution of silver nitrate [23] for 3 minutes.[24] Rinse in water and compare the two portions of the test strip at once in white artificial light or in subdued daylight. The presence of hypo is indicated by a yellow-brown stain on the portion immersed in the silver nitrate solution. The presence of hydrogen sulfide in the water invalidates the test as the paper will discolor regardless of the amount of hypo present.[25]

Hypo Eliminators.—Many substances have been recommended at various times as a means of reducing the time of washing by converting the hypo into compounds more soluble in water.[26] Among the substances which have been recommended for this purpose are lead acetate, zinc hypochlorite, hydrogen peroxide, ammonium persulfate, potassium permanganate, potassium percarbonate, sodium carbonate and bicarbonate, ammonia and ammonium or sodium hydroxide.

Under ordinary conditions, there is no need of a hypo eliminator with negative or positive materials on film or glass, as the hypo can be removed completely in a reasonable time by washing in water, if efficient methods are employed. If it is necessary to reduce the washing time, a hypo eliminator may be useful. After the negatives have been washed for ten minutes, they may be placed for three minutes in a 0.3% solution of ammonium hydroxide and washed for 2 or 3 minutes.

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[20] Lumière and Seyewetz, *Brit. J Phot.* **55** (1908) 417.

[21] Weyde, *Brit. J. Phot.* **82** (1935) 376.

[22] Crabtree, Eaton and Muehler, *J. Franklin Inst.* **230** (1940) 701.

[23] *Note:* Contact with this solution should be avoided as it colors the skin dark.

[24] Clark and Jelley, *Brit. J. Phot.* **76** (1929) 714.

[25] Electrical conductivity methods may also be used for determining the presence of hypo in wash water. Equipment for such determinations is on the market. See also Bender, Electrical Testing for Hypo Elimination. *The Camera* (Phila.) Dec. 1937, p. 364; *Brit. J. Phot.* **85** (1937) 267.

[26] For a bibliography of the literature on hypo eliminators, see Crabtree, Eaton and Muehler, *J. Franklin Inst.* **230** (1940) 701.

With prints, however, the use of a hypo eliminator is necessary to ensure a high degree of permanency as the last traces of hypo are not removable by ordinary washing in water. Experiments in the Kodak Research Laboratories have shown that alkaline hydrogen peroxide will completely oxidize sodium thiosulfate to sulfate which is not adsorbed to the paper fibers and bartya, and unlike the thiosulfate is removable completely by washing in water. Ammonia is the most suitable alkali as, being volatile, the only residue after treatment, is sodium and ammonium sulfate.

The following hypo eliminator [27] is recommended:

Water	400 cc.	16 oz.
Hydrogen peroxide (3% sol.)	125 cc.	4 oz.
Ammonia (3% sol.)	100 cc.	3¼ oz.
Water to make	1 liter	32 oz.

To make 3% ammonia, dilute one part 28% ammonia with nine parts of water.

One gallon (4 liters) of this solution, *which should be used but once,* is sufficient for fifty 8 × 10 prints or their equivalent.

The prints should first be washed for 30 minutes in running water, then placed for 6 minutes in the hypo eliminator and finally again washed for 10 to 15 minutes. The temperature of wash water and solutions should be approximately 70°. The washing times should be increased if the temperature is lower.

With some glossy papers, the change in tone caused by this hypo eliminator may be objectionable. In this case, 15 grains of potassium bromide should be added to each quart (1 gram per liter) of the hypo eliminator.

The slight yellowing of the highlights may be reduced by placing the prints for 2 minutes in a 1% solution of sodium sulfite or acetic acid (1%) upon their removal from the eliminator solution.

Drying.—The problem in drying is to reduce the water content of the negative, or print, as removed from the wash water until it is in equilibrium with the moisture content of the air in which it will be handled or stored. This must be accomplished without causing distortion or local variations in the density of the image, too great a change in density and, in the case of prints, without affecting the color of the image.

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[27] Kodak formula HE-1.

Since the time of drying depends, under given conditions, upon the amount of water to be evaporated, it is clear that the drying time will be lessened if the surface moisture is removed by wiping with a viscose sponge or chamois, or by squeegeeing with a soft rubber squeegee before drying. Wiping or squeegeeing the surface also serves to remove grit or slime which may be attached to the gelatin and to prevent the formation of drops of water which result in drying marks because of the difference in the rate of drying.

Negative materials [28] should be dried in a good circulation of dry, dust-free air at a temperature between 75° and 95° F. (24° to 35° C.). Much higher drying temperatures are possible with prints on developing papers, but rapid drying at high temperature affects the color and density of the image and renders the emulsion and paper stock brittle and easily broken. This is particularly the case with glossy papers dried on ferrotype tins or on a gloss drier.

The time required in drying depends upon the following conditions:

1. *The amount of water absorbed by the gelatin.* This is proportional to the thickness of the swollen film; hence, the higher the degree of swelling the longer the time required in drying. For rapid drying undue swelling of the gelatin should be prevented by maintaining the temperature of the processing solutions and the water used for washing at 65° F. (18° C.) and by using a fixing bath with good hardening properties.

2. *The rate at which the air on the surface of the film is changed.* Air which remains in contact with the surface of the film soon becomes more or less saturated with water vapor and as the degree of saturation increases, the rate of drying diminishes. It is important, therefore, to provide for rapid and continuous renewal of the air in contact with the film so that drying is not retarded. Small volumes of air at high velocity are more effective than large volumes at a low velocity.

3. *The relative humidity of the air.* The ratio between the amount of water in a sample of air and that required to completely saturate it at that temperature is termed the "relative humidity" of the air. The

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[28] Special methods of drying negative materials, page 554.

higher the relative humidity, that is, the more water the air contains, the less it can absorb; thus the relative humidity is an inverse measure of the drying power of the air.

The relative humidity is lowered as the temperature is raised, since the ability of air to absorb water increases with the temperature. The rate of drying, under given conditions, is inversely proportional to its relative humidity and increases with the temperature. The temperature of the drying air should not exceed 90° F. (32° C.) unless the film is specially hardened, or the gelatin is likely to melt.[29] The relative humidity of the air should, if possible, be held approximately at the volume which is in equilibrium with film having the desired moisture content; as film which has been too thoroughly desiccated is brittle. Best results are obtained with air having from 40 to 50% relative humidity.

In general, the density and contrast of the image tend to increase with an increase in the relative humidity and temperature of the drying air. This is due in part to the increased rate of drying and in part to the softening of the gelatin which appears to result in the rearrangement of the grains of silver to produce a higher density.[30]

Uniform drying conditions are essential, therefore, if uniform negative quality is to be maintained.

It is essential that the rate of drying be the same for all parts of the negative, or variations in density are produced. These variations in density, commonly referred to as drying marks, are usually the result of drops of water adhering to the surface of the film during drying. Drops of water are less likely to form on film which has been properly hardened in an acid fixing and hardening bath, or if the surplus water is removed before drying.

Drying marks once formed may be removed by bleaching the image in potassium permanganate and redeveloping. See page 560.

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[29] As for example, a chrome alum stop bath or an alkaline formalin hardening bath.

[30] White, *J. Soc. Mot. Pict. Eng.* **29** (1932) 340.

CHAPTER XII

THE STRUCTURE OF THE DEVELOPED PHOTOGRAPHIC IMAGE

Introduction.—The photographic emulsion was found in Chapter VI to consist of light-sensitive crystals of silver halide in gelatin. These crystals vary in size from ultramicroscope particles to as much as three or four microns, and in various shapes, the most common being triangles or hexagons with the corners rounded off (Fig. 215). In the ordinary film or plate, the emulsion is from 20 to 30 crystals thick and the number involved has been estimated at from 10 to 20 billion per square inch. These crystals vary in *sensitivity* as well as in size, the sensitivity of a crystal being defined as the amount of energy required to make it developable. Consequently, the number of crystals rendered developable upon exposure depends upon the number which absorb sufficient energy to render them developable. The greater the light energy available, i.e., the exposure, the greater will be the number affected.

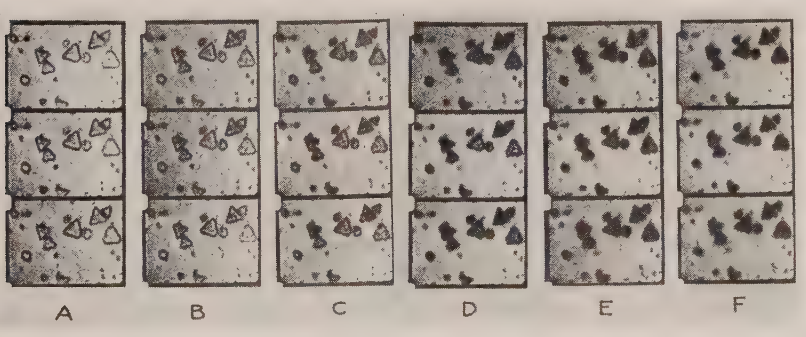
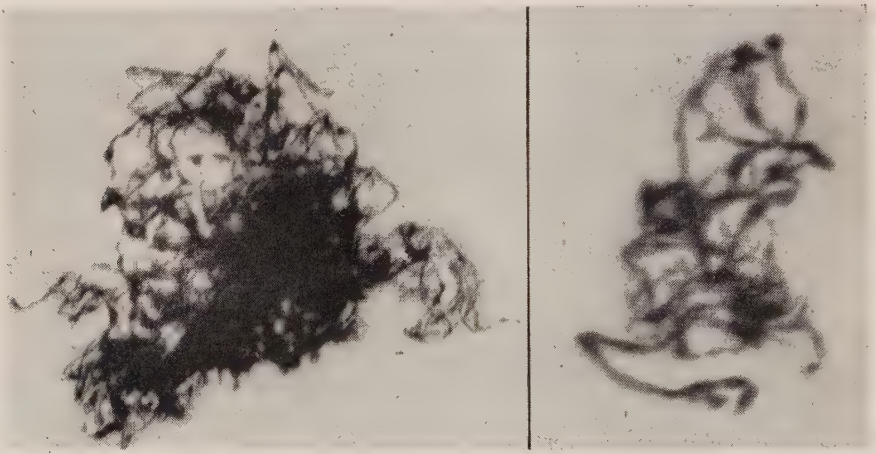


FIG. 215. Photomicrographs of the Development of Crystals of Silver Halide in a Photographic Emulsion. At the extreme left is shown the silver halide grains before development followed from left to right by successive stages of development until the grains of silver halide are completely reduced to metallic silver (extreme right).

Thus the developed image consists of grains of metallic silver formed by the reduction of the developable crystals of silver halide, either wholly or partially, to metallic silver. If development has been carried to completion, all the developable grains are completely converted to metallic silver. In the case of negative materials, however, development is not ordinarily carried to completion; consequently, the image contains many grains of silver which represent crystals of silver halide which have been only partially developed.[1] The silver grains in a negative emulsion vary with the size of the original crystals of silver halide and the degree of development, the largest being on the order of from 4 to 5 microns. They are invisible except at a high magnification (Fig. 215). However, at much lower magnifications, the deposit of silver still possesses a granular structure (Fig. 217). Since the degree of magnification is not sufficient in this case to separate, or resolve, the individual



(*a*) (*b*)

FIG. 216. Photomicrographs of the Developed Silver Grain at a Magnification of 30,000 Times, Made in the Kodak Research Laboratories with the Electron Microscope. The grain in (*a*) has been developed in metol; that in (*b*) in hydroquinone.

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[1] Recent studies of the structure of the developed silver grain at magnifications of 20,000 to 25,000 × with the electron microscope have shown that the particles of silver are not solid but have a filamentary structure, the nature of which varies slightly with different developing agents. Metol and amidol, Fig. 216 (*a*) produce fine filaments; while hydroquinone (*b*) produces coarse filaments. In the fully developed grains of photographic deposit, the filaments are so closely packed that the grain is completely opaque and the filamentary structure is evident only along the edges.

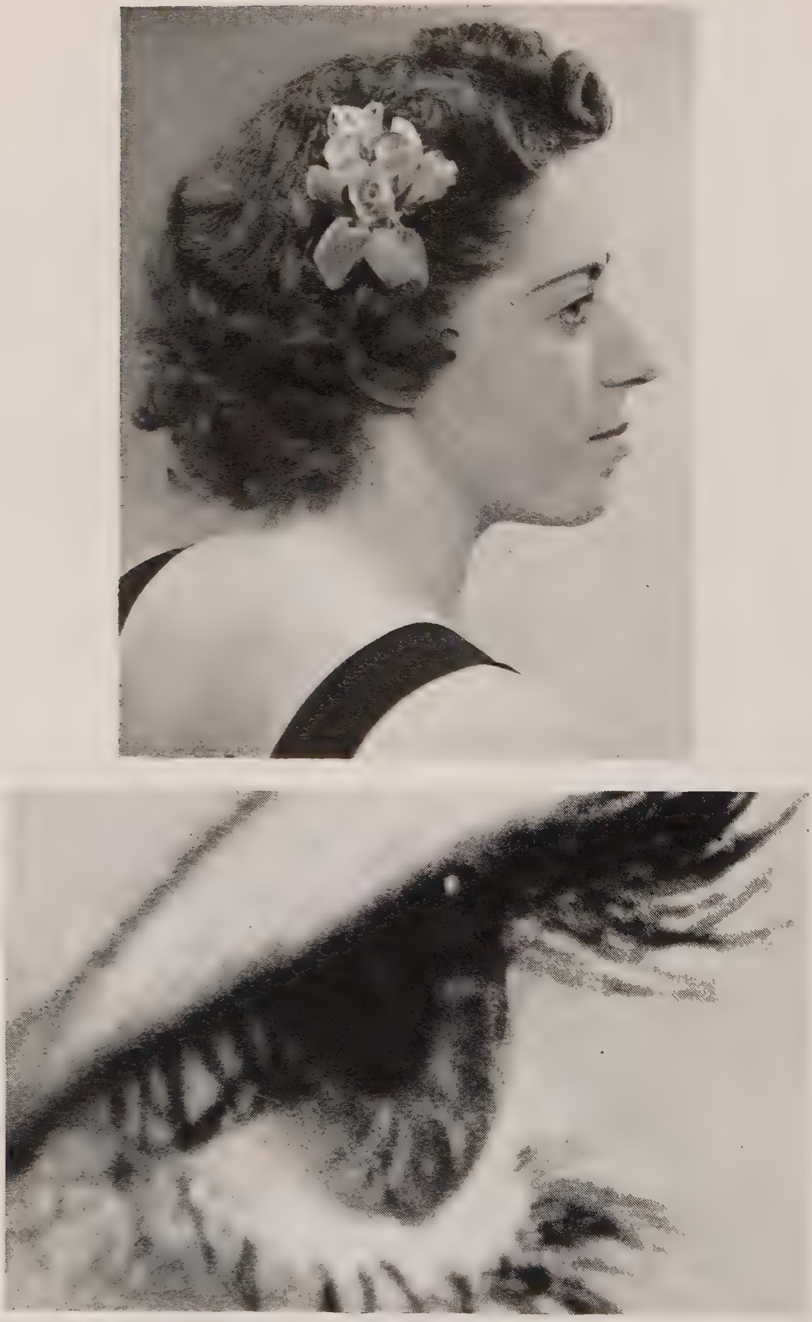
silver grains, it is apparent that they are not uniformly distributed in the gelatin layer but tend to occur in groups or clumps.

The granularity or non-homogeneity of the image, arising from variations in the distribution of the grains of silver, is not restricted to any particular degree of magnification; on the contrary, for every degree of magnification there is a corresponding degree of non-homogeneity. Even at the comparatively low magnifications involved in enlarging, the non-homogeneity of the negative image is evident in the granularity or "graininess" of the projected image (Fig. 218). From this, it is evident that the clumps of silver grains, like the grains themselves, are not evenly distributed in the image.

FIG. 217. Granular Appearance of the Developed Image at a Magnification of 100 ×.

The non-homogeneity of the silver deposit is due primarily to the clumping of the crystals of silver halide in the emulsion, but the scatter of light within the emulsion favors the formation of larger clumps of silver and, in development, causes the action to spread from a grain to others which may be adjacent to it even if these have not received sufficient exposure to make them developable. In this way, the clumping of silver particles is increased beyond that which would naturally occur from the clumping of the silver halide crystals themselves. There is also an optical clumping due to the overlapping of clumps of silver at different depths in the emulsion layer to form a larger aggregate. This is not an important factor except at relatively low densities becoming less as the density increases, since the overlapping of the clumps then results in greater homogeneity.

The Graininess of Photographic Deposits.—The term *graininess* is applied to the degree of non-homogeneity visible at low magnification—as in projection or projection printing—to distinguish it from the non-homogeneity produced by the separation, or resolution, of the individual silver grains which is possible only at much higher magnification. While the two are related, graininess is of concern to every photographer, while the size of the silver grains, the size-frequency, etc., are



(*a*)

FIG. 218. Graininess of the Photographic Image: (*a*) is an Enlargement of a Portion of the Image and Shows the Graininess Evident With Only Moderate Magnification of the Image.

matters which, in general, interest only the emulsion maker, or the physicist.

The first quantitative measurements of the graininess of photographic deposits were made by Jones and Deisch,[2] who designed equipment for measuring graininess in which the non-homogeneity of the density is determined from the distance at which a magnified image of the deposit must be placed to appear homogeneous. Similar apparatus has since been designed by Jones and Hardy[3] and by Lowry.[4]

The use of a comparison microscope in which the magnification of the silver deposit is altered until the degree of non-homogeneity is the same as that of a standard test object has been described by Conklin.[5]

Suggestions have been made "that the Callier coefficient—i.e. the ratio of the diffuse to the specular density—be used as a measure of graininess[6] but has been shown by Lowry to be unreliable.

Microdensitometer traces, i.e., the line representing the variations in density as measured by a microdensitometer, have been used by Dunham[7] and by Mees to indicate the relative graininess differences of films

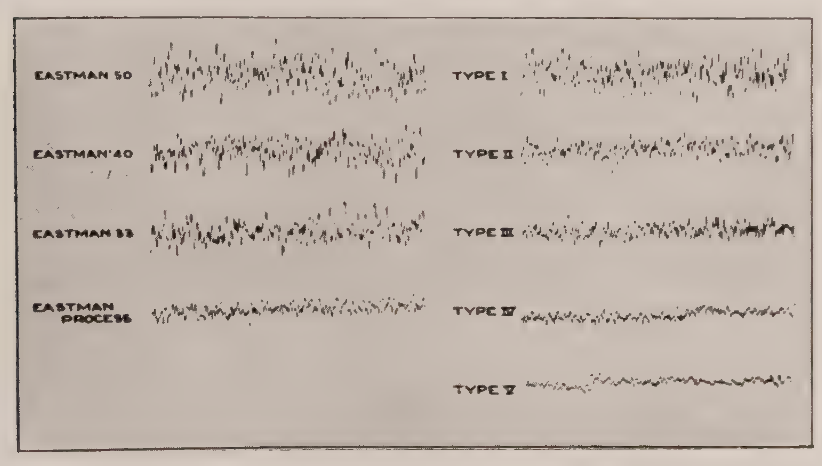


FIG. 219. Microdensitometer Traces Showing Graininess Differences of Typical Negative Materials.

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[2] Jones and Deisch, *Brit. J. Phot.* **67** (1920) 689, 706.

[3] Jones and Hardy, *Trans. Soc. Mot. Pict. Eng.* No. 14 (1922) 107.

[4] Lowry, *J. Opt. Soc. Amer.* **26** (1936) 65.

[5] Conklin, *Trans. Soc. Mot. Pict. Eng.* **16** (1931) 159.

[6] Jones and Deisch, *loc. cit.* Threadgold, *Phot. J.* **72** (1932), 348. Kuster, *Phot. Korr.* **70** (1934) 17.

[7] Dunham, *Die Anwendung der Photographie in der Astrophysik*, p. 287.

and plates for astronomy and spectrography. In Fig. 219 [8] are shown microdensitometer traces showing the relative graininess of several plates varying in speed from a process material to one of comparatively high speed.

A graininess meter employing photographic recording of the microdensitometer readings and an integrator to reduce these tracings to a numerical measure of graininess has been described by Goetz.[9]

Crabtree employed enlargements having the same density and contrast, made on the same paper and under the same conditions.[10] This method has the advantage that it corresponds with the conditions under which graininess is of concern to the photographer. Relative values for graininess are obtained from the distance at which the graininess of the enlargement just disappears.

If this method is followed, the following precautions must be strictly observed:

1. *The images must be carefully focused.* Graininess is very dependent on sharpness of the image and any procedure which tends to diminish this sharpness, such as lack of critical focusing, movement during exposure, or the use of a lens of low resolving power, will also tend to diminish the graininess, and therefore vitiate the graininess comparison.

2. *Prints must be matched exactly with regard to highlight and shadow densities since the appearance of graininess is very dependent on the density contrast of the print.*

3. *The conditions of comparison must be held constant.* This means that the test object must remain uniformly lighted, the camera focus

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[8] Mees, *Photographic Plates for use in Spectroscopy and Astronomy,* Eastman Kodak Company.

[9] Goetz, *Phot. Tech.* **1** (1939) Sept. p. 21.

[10] Crabtree, *Brit. J. Phot.* **86** (1939) 3, 19, 39.

Goetz, Gould and Dember—Objective Measurement of the Graininess of Photographic Emulsions. J. Soc. Mot. Pict. Eng. **34** (1940) 279.

Reinders and Beukers—Fine Grain Developers and a Method of Determining the Graininess of Photographic Plates. Phot. J. **78** (1938) 192.

Selwyn—Experiments on the Nature of Graininess. Phot. J. **79** (1939) 513.

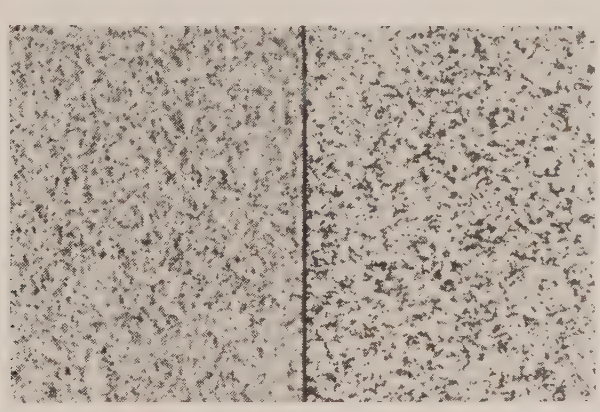
Threadgold—The Callier Coefficient and Its Relationship to Graininess. Phot. J. **79** (1939) 524.

Varden—A Few Considerations on the Problem of Graininess. J. Phot. Soc. Amer. **6** (1940) 9.

should not be changed, the same emulsion should be used, the developing conditions should be identical, the focus of the enlarger should not be altered, and matched prints must be obtained by similar development of paper of the same batch number.

Factors Affecting the Graininess of Photographic Images.—Among the factors affecting graininess are:

1. *The emulsion.* The primary cause of graininess is the clumping of the grains of silver halide in the emulsion. Important factors in the clumping of the silver halide grains would appear to be the average grain size and the size-frequency, i.e., the relative number of grains of each size present. In general, it appears that the tendency towards clumping is at a minimum and therefore grainine sss is lower, the more nearly uniform in size the grains of an emulsion and the smaller the average grain size. The manufacturers of sensitive materials have succeeded in recent years in producing emulsions with greatly reduced graininess, but the methods employed have not been disclosed.



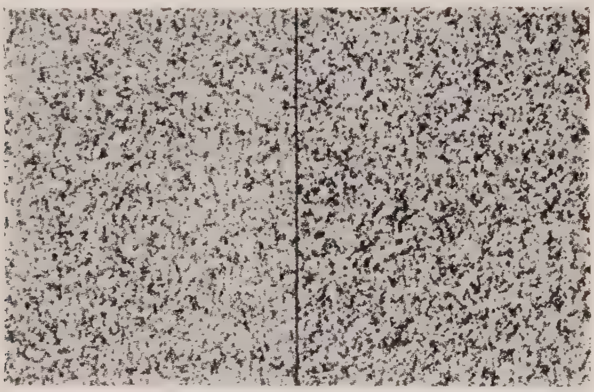
Gamma
0.35

Gamma
1.09

FIG. 220. Showing Graininess of Images of Equal Density Obtained from Negatives Given Different Exposures and Developed for Different Times Producing Low and High Gammas. Note that the Print from the Low Gamma Negative is less Grainy (Crabtree).

2. *The density of the silver deposit.* Under given conditions, and with all emulsions, the graininess increases with the density up to a maximum which varies between 0.3 and 0.6, depending upon the emulsion and the conditions of development. From this, it is evident that

the various tones of the image exhibit varying degrees of graininess according to their density. Graininess is always more in evidence in the lighter tones of the positive and in an area of relatively uniform brightness such as the sky or the face. Factors which keep the density of the negative as low as is consistent with good negative quality; namely, the avoidance of over-exposure and development to a low gamma, are desirable in securing fine-grain images.



Density 0.34 Density 1.98

FIG. 221. Images of Equal Density Printed from Negatives of Different Density. Note that the Denser Negative Gives the Granier Image (Crabtree).

3. *The degree of development or gamma.* Since the development of a grain of exposed silver halide is progressive, starting from a center, or nucleus, on the silver halide grain and continuing until the entire grain is reduced to silver, it is evident that if development is arrested at an early stage, the grains will be only partially developed and the particles of developed silver comprising the image will be smaller, and the clumping less, than if developing is carried nearer to completion. Since the visibility of the grain and grain clusters, which determines the graininess of the image, is proportional to their size, it is apparent that a developed image of any given density obtained in one case by full exposure and a low degree of development will, in general, exhibit less graininess than one which has received less exposure and has been developed to a higher gamma.

4. *The composition of the developer and conditions of developer.* Much has been published in recent years regarding fine-grain developers

and development. A great deal of this information is based upon theories and data of questionable validity and many of the claims cannot be substantiated in practice. Quantitative data is lacking on many processes and methods which have been highly publicised and the entire subject is one in which quantitative investigation is sadly needed. In general, however, it appears that a substantial improvement in graininess is possible in development only with developers of low reduction potential, or possessing a high solvent action on silver halide and at the expense of emulsion speed. Attention should be called to the fact that the lack of homogeneity, or graininess, in a projected image depends to a considerable degree upon the character of the illumination on the negative. See Page 624.

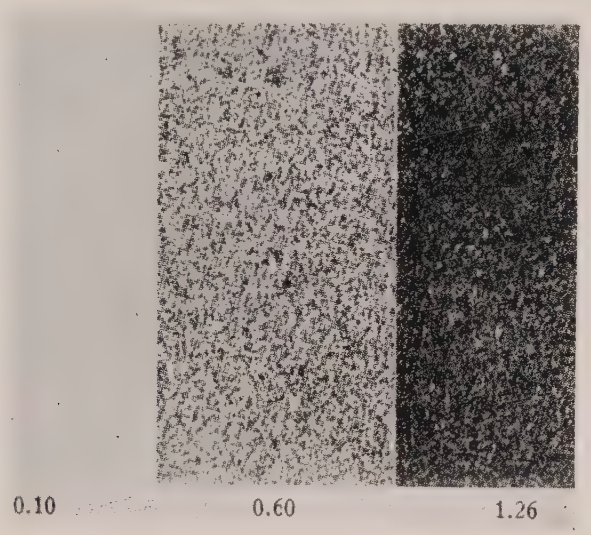


FIG. 222. Silver Deposits of Different Density Showing that the Maximum Graininess Occurs at a Density of from 0.6 to 0.8 (Crabtree).

The Sharpness of the Photographic Image.—The sharpness with which an image is recorded by the sensitive material is an important consideration in many fields of photography, especially in miniature camera work where the negative must be greatly enlarged and any unsharpness in the negative is likely to be evident in the enlargement; in astronomical photography, where star images in clusters must be sharply defined in order to be clearly separated; in aerial photography, where sharpness is required in fine detail; in photomicrography and in many other fields of applied photography.

Since the photographic image is not homogeneous, being composed of grains of metallic silver grouped in clumps, it is evident that even with an exposure just sufficient to form an image, the line marking the boundary between an exposed and an unexposed area will, upon sufficient magnification, be found to have an irregular edge. This is shown in Fig. 223 which is a photomicrograph of the image formed by the edge of a razor blade in contact with a positive emulsion which has been exposed with parallel light. With increased exposure (right) the line becomes still less sharp. The diffusion of the image observed

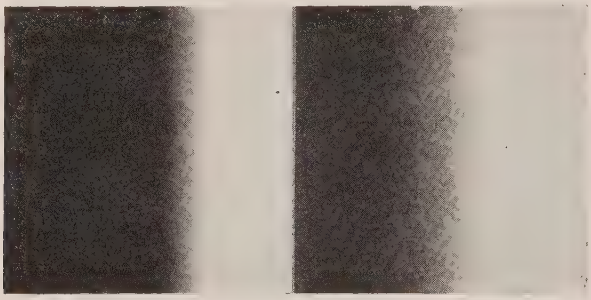


Fig. 223. Low-Power Photomicrograph of the Image of a Razor Blade Exposed in Contact with the Emulsion. The Result of Increased Exposure is Shown at the Right.

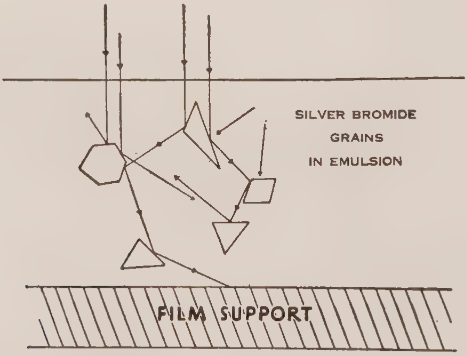


Fig. 224. Diagram Illustrating the Scatter of Light by Grains of Silver Halide in the Emulsion.

with increased exposure is due to the scatter of light within the emulsion which results in light sensitive crystals of silver halide along the edge covered by the razor blade and, therefore, not directly exposed to the incident light, being exposed by light reflected from, or diffracted by other crystals of silver halide which are within the exposed area (Fig. 224). The greater the exposure, the more pronounced the spreading of the image beyond the boundary of the exposure on the surface.

If by means of a micro-densitometer, an instrument designed to measure the density of very small areas, the density of the diffused image produced by the scatter of light within the emulsion is measured at regular intervals from the boundary of the exposed area to its extreme limit, and density is plotted as a function of the distance, a curve is produced which has the same shape as the familiar *D* log *E* curve. In other words, the *D* log *E* curve of an emulsion is the same as the "sharpness" curve, except that the abscissae are compressed by a constant factor.[11] This would indicate that emulsions having a high gamma, a long straight-line portion and a short "toe" or "foot" would be the best for maximum image sharpness.

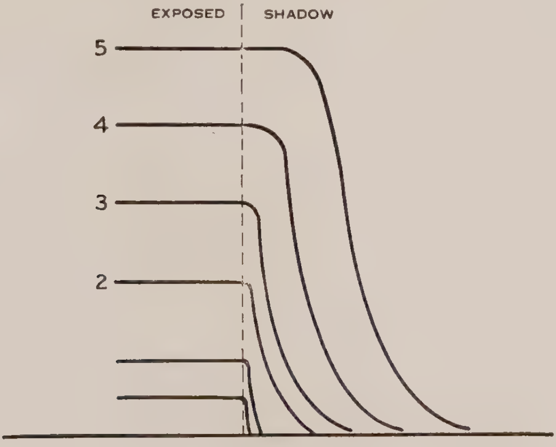


Fig. 225. Density Gradient at the Edge of An Image.

The degree of penetration of the emulsion by light and hence the amount of scattering varies with the wave length. In general, the

[11] Goldberg, *Phot. J.* **36** (1912) 300. Tugman, *Astrophysical J.* **42** (1915) 331.

Mendelssohn—The Diminution of Illumination at the Edge of an Image. Phot. J. **78** (1938) 128.

maximum sharpness occurs in the ultra-violet, decreasing rapidly to a minimum in the blue-green and increases somewhat in the orange and red (Fig. 226), but there is some variation with different emulsions.

It would appear, therefore, that in most cases the highest sharpness with any particular emulsion is obtained when the developed image lies chiefly on the surface of the emulsion layer. So far as the sharpness of the image is concerned, it does not appear to matter whether the surface image is the result of low exposure, the use of a thin emulsion coating, the incorporation of a dye in the emulsion to prevent the penetration of light into the lower layers or by development in developers which act chiefly on the surface of the emulsion layer.

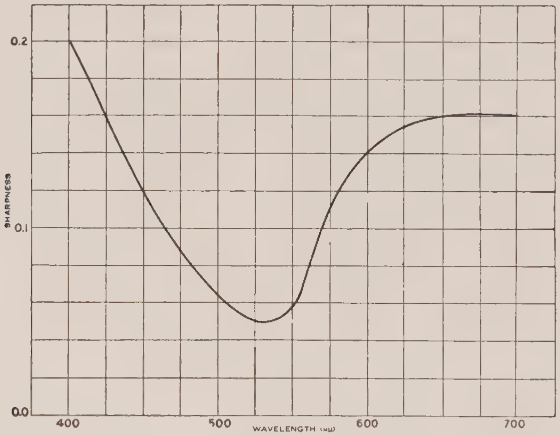


Fig. 226. Curve Showing the Variation of Sharpness with the Wave-Length of the Exposing Light.

Yellow dyed emulsions have been employed to secure maximum sharpness as in films designed for the duplication of motion picture negatives and in plates for spectroscopic work; however, it is necessary in such cases to use emulsions of high contrast as the incorporation of a yellow dye reduces the density and contrast by limiting the penetration of light.[12]

Halation.—The halo which is sometimes observed in photographic images of bright objects or sources of light is known as *halation*. Halation is another example of the spreading of the image beyond the bounds of the exposure (Fig. 223) and is produced when light is reflected back into the emulsion from the rear of the support so as to form a secondary image (Fig. 227). Halation and irradiation usually occur together and, while the former may be almost totally prevented by coating the rear of the emulsion support with a light-absorbing layer or *backing,* irradiation remains unaffected. It is probable, therefore, that most cases of halation are due in large measure, if not wholly, to irradiation: i.e., scattered light in the emulsion.

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[12] *Motion Picture Laboratory Practice,* Eastman Kodak Co. 1936.

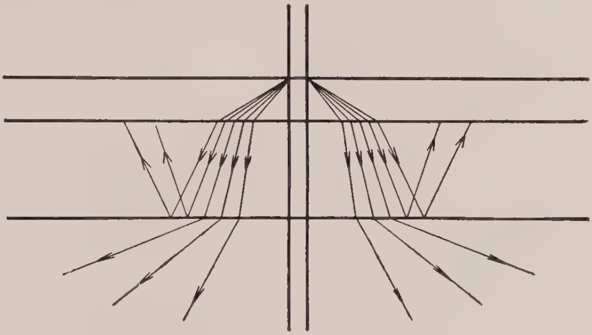


FIG. 227. Diagram Showing How Rays of Light Reflected from the Back of the Support Produce Halation.

The density of the secondary, or halated, image, and to some extent its size, depend upon several factors:

1. *The amount of exposure.* The greater the exposure, or the greater the contrast between the bright object and its surroundings, the more pronounced the halo.

2. *The degree of development.* The greater the degree of development, the higher the density and therefore the intensity of the halo. Developers which act chiefly on the surface or in the upper layers of the emulsion, develop less of the secondary, or halated, image than those which develop the exposed grains next to the emulsion support.

3. *The turbidity and thickness of the emulsion.* The greater the turbidity and thickness of the emulsion coating, the less light it transmits and, therefore, the lower the density of the secondary image under given conditions. A thickly coated film or plate is much less subject to halation than a thinly coated one.

The methods employed to prevent halation may be conveniently grouped under three heads:

1. *Placing a light-absorbing layer, or backing, on the rear surface of the glass or film base.* Backed plates have been an article of commerce

almost as long as the dry plate itself and the value of backed plates in dealing with subjects in which halation is likely to occur is well established. In recent years, backings containing dyes which are decolorized in the developer, or fixing bath, and require no attention in processing have largely replaced the older backing materials which contained a pigment in a water soluble material, such as dextrine or caramel, which had to be removed during development by washing in running water and discolored the developer so that it could no longer be used.

2. *Increasing the amount of light absorbed in the emulsion by double coating.* This has long been popular in the United States where the majority of cut films intended for professional use are double coated; first with a slow, blue-sensitive emulsion and then with the regular negative emulsion. The emulsion next to the support ordinarily plays no part in the formation of the image. It is designed to be as opaque as possible and its only function is to absorb light transmitted by the emulsion coated over it.

3. *Increasing the opacity of the film base.* For motion picture work, a soluble backing is not desirable and instead a grey base film in which the backing is an integral part of the film base is used. The increased density of the negative is compensated for by increase in exposure when printing.

Resolving Power of Photographic Materials.—Closely connected with the spreading of the image, although not wholly dependent upon it, is the resolving power of the emulsion. Resolving power refers to the ability of the emulsion to define sharply or "resolve" fine detail in the image, and may be quantitatively defined as the distance between two closely adjacent images, or lines, which can be rendered separately by the emulsion. It is more conveniently expressed as the reciprocal of this distance; in other words, the greater the number of lines per millimeter an emulsion can reproduce clearly, i.e., the less the distance between the lines, the higher the resolving power. Thus, if two lines are separated by a distance equal to the width of the lines, resolving power may be expressed numerically as the number of lines per millimeter.

KUSTER—An Objective Method for the Determination of Halation. Phot. Korr. **71** (1935) 65, 73; Sci. et Ind. Phot. (II) **6** (1935) 363.

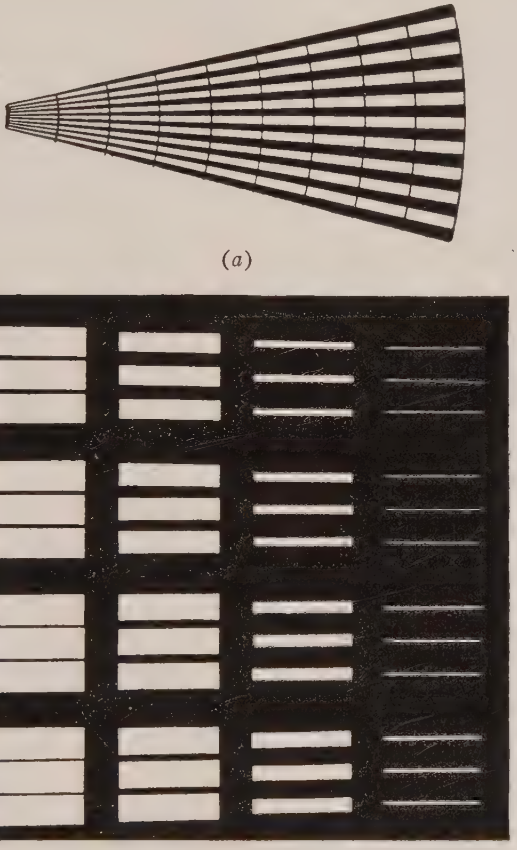
MAUGE—Examination and Measurement of Halation. Bull. Soc. franç. Phot. **14** (1927) 12–30.

NEUGEBAUER—Halation Tests. Photofreund. **9** (1930) 452.

RHEDEN—Halation and Its Prevention. Phot. Rund. **4** (1926) 69.

SAYCE—The Measurement of Resolving Power. Phot. J. **80** (1940) 456.

The resolving power of an emulsion is usually determined by photographing with a well corrected lens, a test object composed of parallel lines of different widths or a fan-shaped grating [13] (Fig. 228).



(a)

(b)

Fig. 228. Design of Gratings Used in Determining the Resolving Power of an Emulsion. (a) Mees, (b) Sandvick.

Factors Affecting Resolving Power.—

1. *The emulsion.* In the case of emulsions blended of fine grains for contrast and course grains for speed, the resolving power varies with

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[13] Mees, *Proc. Royal Society,* **A83** (1909) 10. Tugman, *Astrophysical J.* **42** (1915) 331. Ross, *The Physics of the Developed Photographic Image.* Van Nostrand 1924. Sandvik, *Proc. Seventh International Congress of Photography,* Heffer, Cambridge 1929.

the exposure and the highest resolving power for any speed is obtained with the closest approach to uniformity in grain size. The higher the maximum gamma, the greater usually is resolving power.

So far as color sensitizing is concerned, the best sensitizer for increased resolving power is a green sensitizer whose actual color acts as a minus blue filter. Ideally, the effect of the dye would be to balance the increase in speed from the absorption in the blue and violet. Ordinary yellow dyes improve resolution only by keeping the image on the surface and reducing image spreading.

In general, resolving power increases with decreased graininess and becomes less as the thickness of the emulsion coating increases. If the emulsion coating is too thin, the grains are too scattered to form sharp image edges; if too thick, the image spread is marked. The optimum value lies between these extremes and varies with the emulsion characteristics.[14]

2. *The exposure.* The resolving power tends to decrease with the exposure because of increased spreading of the image.[15]

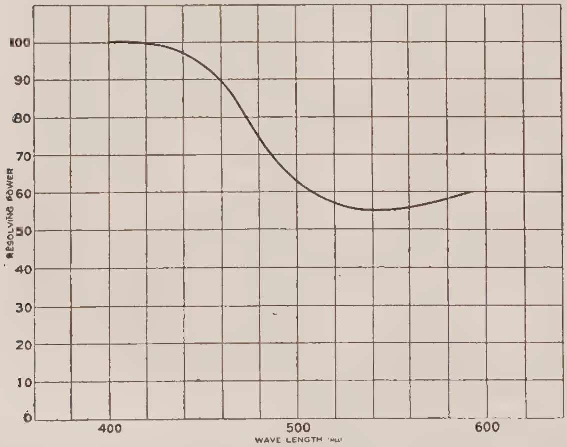

FIG. 229. Curve Showing the Variation in Resolving Power with the Wave-Length of the Exposing Light.

3. *The contrast of the image.* The resolving power with most emulsions and given conditions of exposure and development tends to increase with the contrast of the subject.[16]

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[14] Sandvik, *Proc. Seventh Cong. of Phot.*, Heffer, Cambridge 1929.

[15] Sandvik, *loc. cit.*

[16] Sandvik, *loc. cit.*

4. *The color of the exposing light.* The resolving power varies with the wave length of the exposing light, the general curve representing the relation between resolving power and wave length being very similar to the sharpness curve (Fig. 229).[17]

5. *The developer.* The resolving power appears to vary with the developing agent but the reason for this is not entirely clear. Developing solutions which produce images of high density and contrast, result usually in images with higher resolving power. Fine-grain developers, in general, do not produce high resolving power. Developers which produce a D log E curve with a short steep, toe portion are superior in this respect to those which produce long sweeping curves.[18]

It is probable that the swelling and shrinkage of the gelatin in processing has some effect on resolving power, but no extensive studies of the subject appear to have been made.

Resolving Power of Typical Negative Materials.—The following values are for a subject with a brightness range of 1 : 30, using a light source with a color temperature of 5400° K., the accepted standard for noon sunlight, and development in a borax type developer:

	Lines per mm.
High speed panchromatic film	45
Fine grain film for miniature cameras	55
Positive motion picture film	50
Positive motion picture film (contrast)	70
Micro-file film (contrast developer)	130

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[17] Sandvik, *loc. cit.* Sandvik and Silberstein, *J. Opt. Soc. Amer.* **17** (1928) 107.

[18] Huse, *J. Opt. Soc. Amer.* **1** (1917) 119.

CHAPTER XIII

PHOTOGRAPHIC SENSITOMETRY

Definition and Scope of Sensitometry.—One of the primary concerns of sensitometry is the measurement of sensitivity. However, an adequate measure of sensitivity cannot be obtained without reference to the other characteristics of a photographic material; hence, sensitometry is more completely defined as the quantitative measurement of the response of photographic material to radiant energy.

Moreover, as the effect of exposure becomes apparent only after development, quantitative determinations of sensitivity must involve the measurement of development and its effect on sensitivity.

While formerly of interest only to the manufacturers of photographic materials and those engaged in research, sensitometric methods are now widely employed in the processing of photographic materials, particularly in the motion picture industry, and as time goes on there is little doubt that sensitometric methods will be used more and more in practical photography.

Sensitometric investigations provide a means of determining and expressing quantitatively:

1. The speed, or sensitivity, of a photographic material.
2. The degree of development secured under given conditions.
3. The time of development for a given degree of development.
4. The latitude, or exposure range, of a material.
5. Conditions governing the reproduction of tone.
6. Means of expressing relative contrast and the maximum contrast attainable with a given film or plate and conditions of development.

Reciprocity Effect.—Measurements of the response of a photographic material to light, or other forms of photochemically active radiation, are based fundamentally on the density (or amount of metallic silver) produced under given conditions of development, by an exposure which is measured in terms of the illumination acting on the sensitive material multiplied by the time which it is allowed to act.

Bunsen and Roscoe, as a result of their investigations on the darkening of silver chloride papers, established what is called the *reciprocity* *law,* according to which the photochemical effect (or blackening produced) is the product of time and intensity; time being a reciprocal of intensity, or vice versa. It was shown by Abney, however, that the photographic plate does not exactly obey the reciprocity law and that the effect produced by a given exposure depends upon the actual values of intensity and time and not simply on their product.

Following a series of investigations on the relation of time and intensity in photographic exposure, Schwarzschild suggested that the relation might be written as

$$E = It^p,$$

where E stands for the effective exposure, or photographic effect; I and t for intensity and time, and p a constant which Schwarzschild thought to be independent of the actual light intensities and of the sensitive material.

Later work has shown that for each plate there is an optimum intensity of light which produces the greatest developable effect. The value of this optimum intensity depends chiefly on the speed of the plate or film. In the region of the optimum intensity, the reciprocity law is approximately followed; only at lower intensities does Schwarzschild's rule hold. It has also been shown that the maximum density developable for a given exposure depends upon the intensity of light acting, decreasing as this becomes less. Lastly, the magnitude of the reciprocity failure increases greatly as the emulsion speed, or sensitivity of the emulsion, decreases and is apparently greater with color-sensitive than with non-color-sensitive materials.

Closely connected with the failure of the reciprocity law is the "intermittency effect," discovered by Abney, who found that the photographic effect of an intermittent exposure is not equal to a continuous exposure for the same time but differs by an amount which depends upon the degree of intermittency and the speed of the sensitive material.[1]

[1] Abney, *Treatise on Photography,* p. 391.

Jones and Huse—On the Relation between Time and Intensity in Photographic Exposure. J. Opt. Soc. Amer. **7** (1923) 1115.

Jones, Huse and Hall—Relation between Time and Intensity in Photographic Exposure. J. Opt. Soc. Amer. **12** (1926) 321–348.

Jones and Webb—Reciprocity Law Failure in Photographic Exposures. J. Soc. Mot. Pict. Eng. **23** (1934) 142–159.

Toy—Relation between Time and Intensity in Photographic Exposure. Brit. J. Phot. **73** (1926) 704.

Recently it has been found that an intermittent exposure produces the same result as a continuous exposure of the same duration, if the degree of intermittency is above a certain critical level which *varies with the intensity level.*[2]

Exposure of the Material for Sensitometric Purposes.—If the response of a material to light or other forms of radiant energy is to be determined quantitatively, it is obviously necessary to provide (1) a means of producing a series of accurately known exposures, and (2) development under measurable and standardized conditions.

The exposure of the material involves: (1) the establishment of a standard light source of known intensity and spectral composition, and (2) a means of producing a series of known exposures on the photographic material.

Light Sources.—Candles, and lamps burning liquid pentane, amyl acetate and acetylene have been employed as standards, but standardized incandescent electric lamps are used almost exclusively at the present time. It is necessary to calibrate such lamps accurately for luminous intensity and spectral distribution (color temperature) in a testing laboratory. Inasmuch as both of these factors depend upon the temperature of the filament, which in turn depends on the current flowing through the lamp, it is necessary to control with a high degree of precision the electric supply from which the lamp is operated in order to maintain a suitable standard.

The spectral distribution of energy in the radiation emitted by incandescent electric lamps of the type suitable for use as standards is quite different from that of sunlight. Since the radiation from an incandescent standard lamp is relatively richer in the long-wave region, a blue-violet filter is required to secure radiation approximating that of

[2] Webb, *J. Opt. Soc. Amer.* **23** (1933) 157.

DAVIS AND GIBSON—Artificial Sunlight for Photographic Sensitometry. Proc. Seventh Int. Congress of Phot. London. 1928.

DAVIS AND NEELAND—Variation of Photographic Sensitivity with Different Light Sources. Bur. Stand. J. Res. **7** (1931) 843.

DAVIS AND NEELAND—Variation of Photographic Sensitivity with Different Light Sources. J. Soc. Mot. Pict. Eng. **18** (1932) 732.

MEES AND SHEPPARD—Investigations on Standard Light Sources. Phot. J. **50** (1910) 287; Brit. J. Phot. **57** (1910) 627.

WALSH—Standards of Light for Photographic Sensitometry. Phot. J. **65** (1925) 52.

Report of the Optical Society of America Committee. Unit of Photographic Intensity. J. Opt. Soc. Amer. **12** (1926) 567.

noon sunlight. To attain a color temperature of 5400° K, the figure adopted as a standard for noon sunlight, with the highest precision, a liquid filter is required; however, for practical purposes dyed gelatin filters such as the Wratten No. 79, 78 or 78-AA are quite satisfactory.

Sensitometers.—Since exposure is defined as the product of the illumination on the photographic material (in candle-meters) and the time (in seconds), or

$$E = i X t ,$$

a series of exposures may be produced by varying either factor while keeping the other constant. A series of exposures produced by variation of the intensity acting on different portions of the photographic material is termed an *intensity scale;* a scale produced by varying the time of exposure is termed a *time scale.*

An intensity scale may be produced in several ways:

1. *Absorbing media.* This method consists in the use of a series of densities which, when placed between the source of illumination and the sensitive material, vary the illumination in accordance with the transmission of the different steps. Such "step wedges" are made of pigmented gelatin following the procedure originally published by E. Goldberg [3] or are calibrated photographic copies of such wedges. While useful for preliminary or routine sensitometric investigations not requiring a high degree of accuracy, wedges of this type are not sufficiently reproducible or free from selective absorption to be suitable for work of high precision.

2. *Deforming lens systems* (*Optical wedge methods*). The term, optical wedge, is applied to an intensity scale produced by means of a stepped diaphragm used in conjunction with a cylindrical lens. The basic principle is shown in Fig. 230. The stepped diaphragm shown in detail at the left, is placed next to a uniformly illuminated opal glass plate. The cylindrical lens produces an image of the diaphragm on the sensitive material as a series of steps of equal width but varying in intensity with the length of each step. The first to utilize this principle was Guilloz.[4] It was improved by Callier [5] but the image was rather small. This type of sensitometer has been revived by McFarlane in an instrument designed for the sensitometry of developing papers.[6]

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[3] *Brit. J. Phot.* **57** (1910) 642, 648.

[4] *Comptes Rendus* **148** (1909) 164.

[5] *Phot. J.* **37** (1913) 242. *Brit. J. Phot.* **60** (1913) 972.

[6] *J. Franklin Inst.* **228** (1939) 445. Also, *Kinder-Zeit. fuer Instrumentkunde* **10** (1936) 393.

3. *Methods based upon tubes.* The tube sensitometer (Fig. 231) consists of a number of tubes, or cells, having small openings in one end; the sensitive material is placed at the other, which is left open. Thus, the light reaching the portion of the sensitive material exposed at the base of each tube varies as the size of the open area at the other end. The chief objection to sensitometers of this type is the limited range

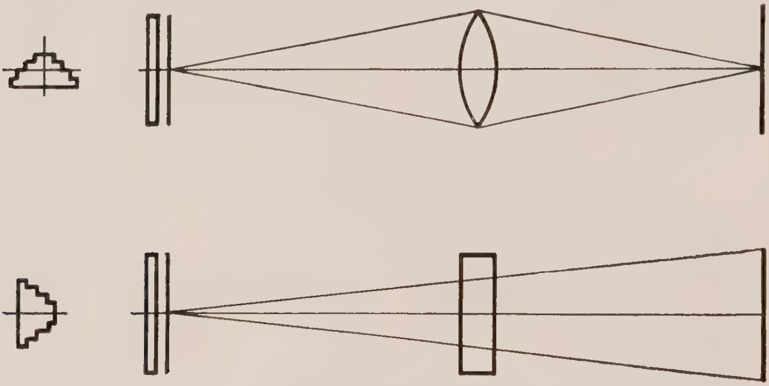


FIG. 230. Optical System Used in Producing an Intensity Scale of Exposures. The Upper Diagram Shows the Cylindrical Lens and Associated Light-Modulation System in Cross-Section. The Lower Shows How the Aperture Plate and Lens are Disposed when Viewed from Above.

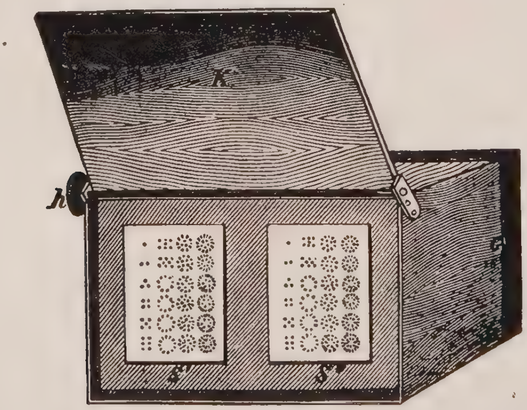
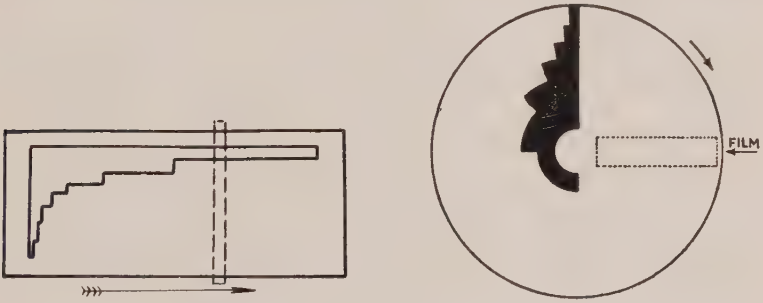


FIG. 231. Tube Sensitometer. An obsolete type of this instrument designed by Vogel. Eder, Ausführliches Handbuch der Photographie.)

in exposure obtainable without resorting to very long tubes of large diameter.[7]

Time Scales.—Time scales are produced by interposing between the light source and the photographic material a continuously moving opaque plate with a series of slits whose lengths vary in accordance with the exposures desired. The shutter may be rectangular with longitudinal slits moving in a straight line (Fig. 232a) or angular openings in a circular disk (Fig. 232b), which is rotated in front of the sensitive material. In the example shown there are nine apertures whose lengths increase logarithmically by consecutive powers of two. Thus, the relative exposure for each aperture from the shortest to the longest is:



(*a*) (*b*)

Fig. 232.

Aperture	1	2	3	4	5	6	7	8	9
Relative exposure	1	2	4	8	16	32	64	128	256

In some cases, a series of exposures with a lower order of progression is desirable and this has led to the adoption in many sensitometers of a scale of exposures increasing as the power of the $\sqrt{2}$ or,

1 1.41 2 2.82 4 5.64 8 etc.

It is obvious that if a disk of the type shown in Fig. 232b is rotated, an exposure time greater than that required for one revolution of the disk results in an intermittent exposure. In other words, the total time of exposure for each aperture is the sum of the exposures produced with each revolution of the disk. The photographic effect of a series of intermittent exposures, however, is not the same as a continuous exposure of the same duration, but varies with the length of exposure, the number of separate exposures, and the photographic material.

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[7] *Eder's Handbuch* **12** p. 412. Jones, *Photographic Sensitometry.* 2nd Ed. Eastman Kodak Co. 1935. Bornemann & Tuttle, *J. Opt. Soc. Amer.* **32** (1942) 224.

The errors resulting from an intermittent exposure may be avoided by rotating the disk more slowly so that the necessary exposures are obtained with a single revolution. If the time required for one revolution of the disk is relatively long, a clutch may be used to engage the driving mechanism which rotates the disk at a constant speed throughout one revolution, at the completion of which the clutch is automatically disengaged and the disk is brought to a stop. This procedure is impractical if the time for one revolution is short, as it is difficult at a high speed to stop and start the disk, or to rotate it at a uniform speed. In this case, the disk is rotated continuously at the required speed and an electrically operated shutter is provided which is so controlled that it remains open for only one revolution of the disk.

No useful purpose would be served by a lengthy description of the different sensitometers based upon these general principles; instead, reference will be made to only one, the Eastman Sensitometer II-b, which is on of the best known and most widely used.

The instrument is shown in detail in Fig. 233 which is a partial vertical section through the optical axis of the instrument.

L represents the standard lamp which is the source of illumination. A selectively absorbing filter *F* is placed in the path of the light coming from the lamp in order to modify its spectral composition to the desired quality. A plane mirror *M* reflects the light at right angles, thus illuminating the exposure plane *EP* in which the photographic material is placed. The rotating cylindrical shutter or drum *D*, having 21 exposure slots increasing in length by logarithmic steps from the shortest to the longest, controls the time factor of the exposure incident upon the

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Cady—A New Photographic Sensitometer. J. Opt. Soc. Amer. **29** (1939) 470.

Davis—Experimental Study of the Relation between Intermittent and Non-Intermittent Sector-Wheel Photographic Exposures. Bull. Bur. Stan. Scient. Papers **21** (1926) 95.

Hardy—A Non-Intermittent Sensitometer. J. Opt. Soc. Amer. **10** (1925) 149.

Higson—A Simple Non-Intermittent Sensitometer. Phot. J. **60** (1920) 235.

Jones—A Non-Intermittent Sensitometer. Phot. J. **60** (1920) 60.

Rawling—Exposure Mechanisms. Phot. J. **65** (1925) 64.

Mees and Sheppard—Instruments for Sensitometric Investigation. Phot. J. **44** (1904) 200. (With excellent bibliography to that date.)

adjacent steps of the exposure scale. The exposure plane is equipped with suitable guides so that two strips of 35 mm. motion picture film may be placed in position and exposed simultaneously. A platen *PL,* when pulled down, serves to hold these strips accurately in the exposure plane during exposure.

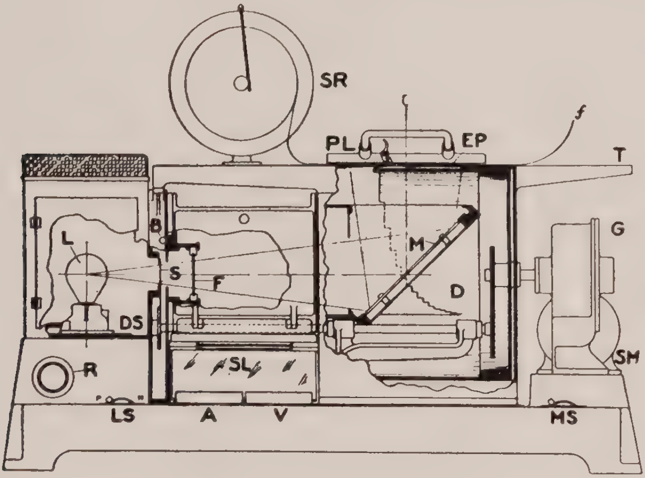

FIG. 233. Cross-Section of the Eastman IIb Sensitometer.

The drum is driven at a constant angular velocity by a synchronous motor *SM.* Through a reduction gear *G,* the motor turns the drum at 12 r.p.m. when operating on a 60 cycle line, or at 10 r.p.m., on a 50 cycle line.

When the machine is started by throwing the master switch *MS,* the drum revolves continuously. Exposures are made by means of the shutter *S,* operated by a one-turn mechanism. Upon pressure of the release button *B,* this shutter opens while the photographic material is protected from the exposing radiation by the opaque portion of the drum, and closes as soon as the slots in the drum have passed the exposing plane.

Developers and Development.—Since the effect of exposure becomes apparent only after development, it is evident that the response of a photographic material is in part dependent upon the conditions of development which must be standardized if accurate and reproducible results are to be obtained. In establishing standards for developers and conditions of development, consideration will naturally be given to the purpose for which the work is done. Since it is well known that many of the characteristics of an emulsion are profoundly modified by the constitution of the developer,[8] it is evident that, if the work is done to supply information on the characteristics of material for practical purposes, the standards adopted must be those of practical photography; on the other hand, if the object is to study the inherent differences in emulsions, to enable the manufacturer to maintain a uniform product, or for the purpose of establishing a national or international standard reproducibility, color of image, freedom from fog, sensitivity to changes in bromide and similar considerations alone need to be taken into account and these may result in the adoption of a developer and conditions of development quite different from those of practical photography.

The developer characteristics desirable in a standard developer for sensitometric work are:

1. *The deposit should be neutral;* i.e., non-selective absorbing.
2. *Freedom from fog* in the absence of an alkaline bromide or other restrainer.
3. *Energy sufficiently high* to produce good density, contrast, and speed.
4. *Relative insensitivity to an alkaline bromide* so that the results will not be affected appreciably by the presence of free bromide in the emulsion.
5. *Reproducibility;* i.e., freedom from unordered variations in the purity of the substances employed and conditions affecting the activity of the solution.

The Seventh International Congress of Photography recommended the following paraminophenol formula:[9]

p-aminophenol hydrochloride	7.25	gm.
Sodium sulfite (anh.)	50	gm.
Sodium carbonate (anh.)	50	gm.
Water to make	1000	cc.

because of the grey (non-selective absorption) deposit, freedom from fog and its relative insensitivity to alkaline bromide so that the results

[8] Clark, *Phot. J.* **65** (1925) 76.

[9] Sheppard and Trivelli, *Proc. Seventh Int. Cong. of Phot.* (1928) p. 174.

Davis and Neeland—Developers and Sensitivity. Bur. Stand. J. Res. **11** (1933) 379.

Sheppard—The Stability of pH of Standard Paraminophenol Developer. Proc. Ninth Int. Congress of Phot. Paris, 1935. Sci. et Ind. Phot. (II) **6** (1935) 400.

are not materially affected by the presence of free bromide in the emulsion.

The following formulas were suggested as standards by the Committee on Standardization in the field of photography, American Standards Association, but have not received final approval:[10]

	1		*2*	
Monomethylparaminophenol sulfate. .	2.0 gm.	8.8 gr.	2.0 gm.	8.8 gr.
Sodium sulfite (anh.).	50.0 gm.	220.0 gr.	80.0 gm.	350.0 gr.
Hydroquinone.	4.0 gm.	17.5 gr.	4.0 gm.	17.5 gr.
Sodium carbonate (anh.).	6.0 gm.	26.2 gr.	4.0 gm.	17.5 gr.
Potassium bromide.	0.75 gm.	3.0 gr.	0.5 gm.	2.2 gr.
Air-free distilled water to.	1.0 liter	10.0 oz.	1.0 liter	10.0 oz.

The first formula is recommended for roll film and film packs; the second for miniature camera films.

In the development of material for sensitometric purposes, efficient agitation of the developer is highly important in order that the developer-reaction products may be removed from the immediate vicinity of the film and distributed in the solution to prevent non-uniform development. The methods developed to attain this end involve:

1. In tanks:
    - *a. Mechanical rotation* of the exposures in the developing solution. It is difficult in this case to prevent directional development.
    - *b. Mechanical stirring of the developer.* The difficulty with this procedure is to insure that all parts of the solution will receive the same agitation.

[10] *J. Opt. Soc. Amer.* **31** (1941) 87.

Bloch and Horton—Mechanical Developing Appliance for Sensitometric Work. Phot. J. **68** (1928) 352.

Clark—Uniform Development. Phot. Tech. **2** (1940) Oct. p. 54.

Harrison and Dobson—Note on the Uniform Development of Photographic Plates. Phot. J. **65** (1925) 89.

Sheppard and Crouch—Machine for the Automatic Development of Sensitometric Strips. Proc. Seventh Int. Congress of Phot. London 1928.

Sheppard, Lambert and Atkins—Semi-Automatic Apparatus for the Development of Sensitometer Strips. Phot. Ind. **34** (1936) 988.

Crabtree—Uniformity in Photographic Development. J. Soc. Mot. Pict. Eng. **25** (1935) 512.

Russell, Jones and Beacham—Developing Machine for Sensitometry. J. Soc. Mot. Pict. Eng. **28** (1937) 73.

  c. *Plungers* moving up and down near the surface of the film to create a rapid and highly uniform distribution of the developer over the surface of the film.
  d. *Vacuum flask method.* In this method the film strips are attached with rubber bands to a glass strip which is affixed to the stopper of a Dewar or vacuum flask (Thermos bottle) so as to suspend the strips in the developing solution. The flask is filled until about two-thirds full and the necessary agitation is obtained by (1) giving the flask an oscillatory motion by tilting it from a vertical plane to an angle of about 45° with the horizontal and back again to the opposite side, once each second, and (2) by revolving the flask about its axis once each 5 seconds. This method has been found to produce highly consistent results and has been recommended by both the British Standards Association[11] and the Committee on Standardization in the field of photography of the American Standards Association.[12] The latter recommendation has not received final approval.

2. In trays:
  a. *Hand rocking.* This is fairly satisfactory if vigorous and irregular.
  b. *Mechanical rocking.* Generally unsatisfactory as the action is too regular.
  c. *Roller charged with developer.* The objection to this method is the rapid oxidation of the developer.
  d. *Brushing* the surface of the film with a soft camel's hair brush. This is probably the best so far as uniformity in development is concerned.

The temperature of the developing solution affects not only the rate of development but to a certain extent the speed and possibly other characteristics of the emulsion. The effect is more marked with some developers than others, but necessitates in any case the maintenance of the required temperature as accurately as possible.

Following development, the sensitometer exposures are rinsed in a stop bath of dilute acetic acid to prevent further development and then transferred to the fixing bath. No special precautions are necessary in fixing or washing, but as the density of a photographic deposit depends in part upon the rate at which it is dried, the strips are usually dried in a drying cabinet at a constant relative humidity or by means of alcohol. Alcohol, however, cannot be used for drying acetate film with safety because the base is attacked, nor should a solution containing more than 80% industrial alcohol be used or the gelatin may be rendered milky.

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[11] *Phot. J.* **80** (1940) 341.

[12] *J. Opt. Soc. Amer.* **31** (1941) 87. *Amer. Phot.* (1941) Feb. p. 81; *Brit. J. Phot.* **88** (1941) 153.

The Measurement of Density.—After exposure and development, the next step is to determine the response of the sensitive material to the different exposures. When a photographic material is exposed to light, or other form of radiant energy, some of the grains of silver halide are rendered developable, and upon development, these are reduced to metallic silver. It is evident, therefore, that the amount of silver produced by a given exposure and conditions of development is a measure of the response of the sensitive material. It is also obvious that ordinary analytical methods of analysis would not only be inconvenient but subject to large errors on account of the relatively small quantities of metallic silver involved. Furthermore, such determinations would not provide any real information on the optical properties of the developed image. The relationship existing between the amount of the photo-chemical product (silver) produced by a given exposure under fixed conditions of development and its light-absorbing and transmitting properties was first expressed quantitatively by Hurter and Driffield.[13]

They defined as the *opacity* of the deposit the ratio of the incident to the emerging light; as *transparency,* the reciprocal of this, or the fraction of the incident light transmitted; and as *density* the logarithm of the opacity, or the negative logarithm of the transparency. Thus, in the case of a silver deposit transmitting one-half of the incident light, the transparency is $\frac{1}{2}$, the opacity 2 and density the common logarithm of this or 0.3.

Density, as thus defined, is proportional to the mass of silver per unit area, or $D = pm$, where D is the density, m the mass of silver and p a constant termed the *photometric constant.*

The value of this constant varies to some extent with the developer and conditions of development.[14]

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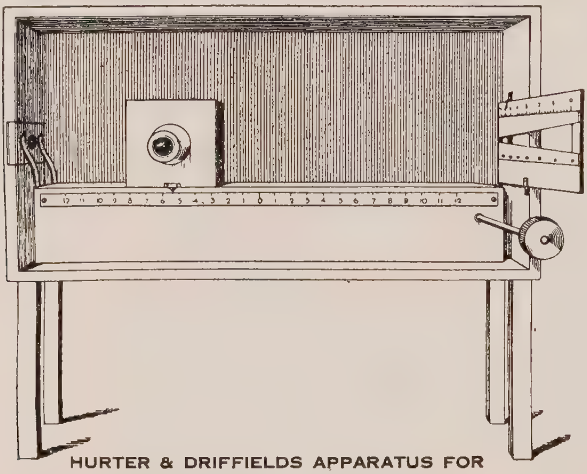
[13] Hurter and Driffield, *J. Soc. Chem. Ind.* **9** (1890) 455.

[14] Meidinger, *Z. physik. Chem.* **114** (1924) 89; Sheppard and Ballard, *J. Franklin Inst.* **205** (1928) 659; *Phot. J.* **66** (1926) 470; Eggert and Kuester, *Kinotechnik* **18** (1936) 381.

Densitometers.—Photometers designed particularly for the measurement of photographic densities are termed densitometers. They may be divided into two classes according to whether they measure the density directly or by comparison with a known density. All densitometers are alike in that they provide means for reducing the intensity of a standard light in a known manner, to match with a similar beam of light which has passed through the density to be measured.



HURTER & DRIFFIELDS APPARATUS FOR MEASURING DENSITY OF NEGATIVES

Fig. 234.

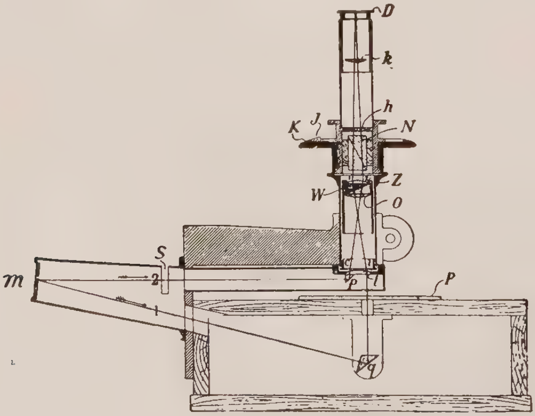


Fig. 235. Path of Light Rays in the Martens Polarization Densitometer.

The intensity of the comparison light may be reduced in a known manner by several methods, as for instance (1) by varying the distance of the light, (2) by the use of adjustable rotating sectors, (3) by polarization and (4) by the use of absorbing material such as the optical wedges mentioned previously (Page 393).

The densitometer employed by Hurter and Driffield in their classical investigations was an instrument of the first class; the well-known bench photometer is based on the law of inverse squares, in which two beams are brought together for comparison on a grease spot. Densitometers with rotating sectors were used by Abney and more recently by Jones. The most widely used instruments, however, have been those employing polarization, and of these the most popular are the Huefner and the Martens.

The construction of the Martens densitometer is shown in Fig. 235. One of the beams of light from an electric lamp placed at *M* proceeds, as shown by the arrow, to the totally reflecting prism *q*, whence it is reflected through the negative *p* and is rendered convergent by the lens *l* passing through the aperture *i* into the actual photometer head. It then passes through the Wollaston prism *W*, and the bi-prism *Z*, then through the Nicol *N* and through the converging lenses *h* and *K* to the eye placed at *D*. The other beam proceeds to the total reflecting prism *p*, thence through the Wollaston prism, the bi-prism, the Nicol, and reaches the eye at *D*. Thus, there is produced at *D* two contiguous fields, one formed by the beam of light which has passed through the density; the other, the comparison beam. The intensity

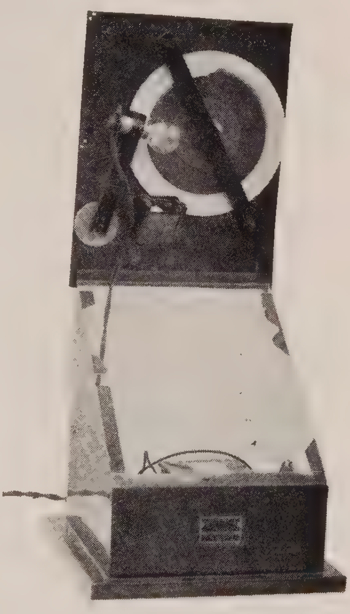


Fig. 236. Eastman Densitometer, Open to Show Light Source and Rotating Circular Density Wedge.

Davies and Owen—A Visual Photometer for the Measurements of Transmission and Reflection Densities. Phot. J. **75** (1935) 128.

Ferguson—The Ferguson Density Meter No. V. Phot. J. **64** (1924) 30; Brit. J. Phot. **71** (1924) 19.

of the latter can be reduced by the rotation of the Nicol *N* and the densities determined from the angle of rotation required to produce equality in the two fields.

Densitometers of class 4 employing calibrated optical wedges are more properly termed density comparators, for their measurement of density consists simply in comparing it with a known density. A number of densitometers of this type are available commercially;[15] the best known in this country is the Eastman Densitometer (Fig. 236).

Photoelectric Densitometers.—Early attempts to use photoelectric cells for the measurement of density were only partially successful, as the cells available were not sufficiently constant in their response-characteristics to enable densities to be measured with the required degree of precision. In several of the earlier experimental densitometers using photoelectric cells,[16] the cell was subjected alternately to two beams of light, one of which had passed through the density to be measured, the other through a calibrated optical wedge. The measurement of the density consisted in adjusting the optical wedge so that the current passed by the cell remains the same, and the gal-

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[15] The Sanger-Shepherd Density Meter, manufactured by the E. S. S. Color Filter Co., London; the Densitometer Filmograph, made by the Etablissements Filmograph, Montrouge, France; Hilger Densitometer, Adam Hilger; Goldberg Densograph, Schmidt and Haensch, Munich.

[16] Dobson, *Proc. Roy. Soc.* **104A** (1923) 248. Toy and Rawling, *Phot. J.* **64** (1924) 189.

Ferguson and Read—A New Reflection Density Meter. Phot. J. **74** (1934) 249.

Goldberg—The Densograph. Brit. J. Phot. **57** (1910) 649; Eder's Jahrbuch, **24** (1910) 226.

Herz—A Particularly Simple Photo-Electric Photometer. Z. wiss. Phot. **37** (1938) 107.

Jones—A Densitometer for the Measurement of High Photographic Densities. J. Opt. Soc. Amer. **8** (1923) 231.

Mees and Shepherd—The Sensitometry of Photographic Plates. Phot. J. **44** (1904) 282 (with excellent bibliography).

Morrison and McFarlane—Eastman Transmission and Reflection Densitometer. J. Opt. Soc. Amer. **25** (1935) 417.

Neumann—A New Densitometer. J. Soc. Mot. Pict. Eng. **32** (1939) 572.

Sanger-Shepherd—Density Meter. Brit. J. Phot. **58** (1911) 926. British Patent 23,429 of 1911.

Sweet—Physical Density Comparator. J. Opt. Soc. Amer. **28** (1938) 349.

Toy and Rawling—Photo-electric Densitometer. Phot. J. **64** (1924) 189; Jl. Scient. Instr. **I** (1924) 362.

Tuttle—A Recording Physical Densitometer. J. Opt. Soc. Amer. **26** (1936) 282. Phot. J. **76** (1936) 495.

vanometer needle shows no change, when the light from one beam is substituted for the other. With this procedure, the absolute value of the photoelectric current is immaterial; it is used simply to indicate equality of illumination (photometric balance) and not directly as a light measuring device.

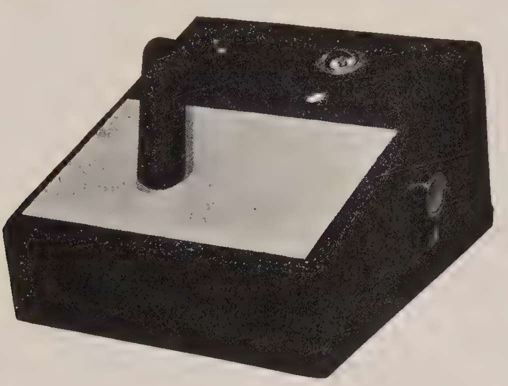

Fig. 237. Photoelectric Densitometer. (National Photocolor Corportion, New York.)

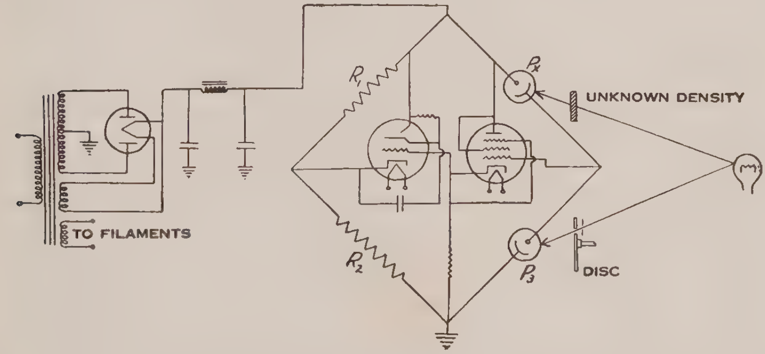

Fig. 238. Wiring Diagram of the Photoelectric Densitometer Shown in the Preceeding Figure.

Several photoelectric densitometers have been introduced, designed primarily for the rapid and convenient measurement of the densities of three-color separation negatives for subtractive printing processes. One such instrument is shown in Fig. 237.[17] This instrument employs a double photoelectric cell balanced circuit and its operation is not affected by fluctuations in the line voltage. Light from a 50 watt lamp is divided by two mirrors so that one beam passes through a calibrated wedge and thence to a photoelectric cell while the other is directed towards a second photoelectric cell located in the movable arm of the instrument. The light, photoelectric cells and wiring diagram are shown in Fig. 238. When the light striking each photoelectric cell is of the same intensity, the current through the photoelectric cells is likewise the same. These two cells are two arms of a Wheatstone bridge, and when these arms balance against the resistors which are the other arms of this bridge, the circuit is electrically in balance. The 78 tube is used as a D.C. amplifier, the output voltage of which actuates the control grid of the electronic indicator. This electronic indicator is biased in such a way that, when the electrical circuit is in balance, the indicator or "magic eye" will close. The value of the density is then read from the calibrated wedge.

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[17] National Photocolor Precision Densitometer, National Photocolor Corporation, New York City.

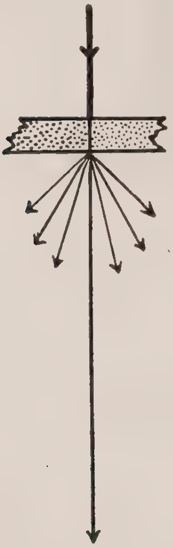

FIG. 239. Diagram Showing How a Ray of Light is Scattered by the Silver Grains of the Image. It is clear that the amount of incident light transmitted will be greater if the scattered light, indicated by the short arrows, is included than if the direct light, indicated by the long arrow, alone is measured.

Optical Characteristics of the Photographic Image.—Certain factors affecting density values as determined by densitometric measurement will now be considered.

In the first place, it may be noted that the photographic image consists of grains of metallic silver imbedded in gelatin. These not only absorb light but scatter a portion of that which is transmitted. Therefore, if the deposit is illuminated by specular (parallel) light (Fig. 239), the amount of light transmitted, and therefore the density as determined by densitometric measurements, will depend upon whether this scattered light is included in the measurement of the density or only the direct, undeviated light. The value of density as obtained with parallel light is termed D parallel or $(D\|)$ and that obtained when the scattered light is included is termed D diffuse, or $(D\#)$. The difference in the two values depends on the optical means employed in measuring the two densities and the light-scattering properties of the image, which in turn depends upon the emulsion and the manner of processing.

The ratio of the diffuse to the specular density is frequently termed Callier's factor after A. Callier[18] who was the first to investigate the scatter of light by photographic negatives. It is sometimes referred to as Q which was the symbol employed by Callier for $D\| / D\#$.

In contact printing, both the scattered and undeviated light reach the positive material; hence, the effective density for contact printing is approximately equivalent to the diffuse density ($D\#$). In projection printing, the lens is at some distance from the image and for this reason cannot collect and transmit all of the scattered light. It is evident, therefore, that in projection the effective density lies between $D\|$ and $D\#$. While in general, it is closer to the latter than the former, for practical purposes it is usually sufficient to determine the diffuse density by the use of a diffused source of illumination secured by placing the density to be measured in contact with opal glass.

If the silver deposit is free from selective absorption, the density values as measured visually are approximately equal to the effective

[18] *Phot. J.* **49** (1909) 200.

BULL AND CARTWRIGHT—The Measurement of Photographic Density. Phot. J. **64** (1924) 180.

BULL AND CARTWRIGHT—An Evaluation of the Light Scattered by Photographic Densities. Phot. J. **65** (1925) 177.

KOERNER AND TUTTLE—Experimental Determination of Photographic Density. Phot. J. **77** (1937) 444.

RENWICK—How Should the Densities of a Photographic Deposit be Measured? Brit. J. Phot. **71** (1924) 65.

PITT—A Note on the Measurement of Specular Density. Phot. J. **78** (1938) 486.

SWEET—Photographic Density Determined by the Contact Printing Method. J. Phot. Soc. Amer. **7** (1941) 126.

TOY—The Standardization of Photographic Density Measurements. Phot. J. **65** (1925) 164.

TUTTLE—Densitometry and Photographic Printing, Illumination of the Negative and Its Effect Upon Density. J. Opt. Soc. Amer. **24** (1934) 272.

TUTTLE—Relation Between Diffuse and Specular Density. J. Opt. Soc. Amer. **12** (1926) 559.

TUTTLE—The Relation Between Diffuse and Specular Density. J. Soc. Mot. Pict. Eng. **20** (1933) 228.

TUTTLE AND KOERNER—The Standardization of Photographic Density. Phot. J. **78** (1938) 739.

printing density. This is generally true in the case of images developed in metol-hydroquinone, metol, paraminophenol or diaminophenol. In the case of pyro and other developing agents producing a stain image, the effective printing density is greater than the value obtained by visual measurement because of the difference in the spectral sensitivity of the eye and that of positive printing materials.[19]

Since an unexposed portion of a sensitometric strip has a measurable density, termed the fog density, it is obvious that a certain fraction of each density is due to fog. The density due to fog, however, is not the same in the exposed steps as in the unexposed portion of the sensitometric strip. The relation between the fog density and the total density is a complicated one, but in general it may be said that as the total density increases, the fog density becomes less and less. This is due to the fact that the by-products released in the development of the exposed silver halide restrain the development of fog. Hence, in the higher densities, the development of fog is restrained to a greater degree than in the lower.

It is the density due to the exposure, and not the total density, which is the true measure of the response of the sensitive material; obviously then measured densities should be corrected for fog.

However, since the fog density is not the same for all densities, the necessary correction cannot be made by subtracting from each of a series of densities a uniform fog value as obtained from an unexposed portion of the strip. Despite the rather complex formulas devised for correcting measured densities for fog,[20] it is usually sufficient to employ densities as measured, neglecting any addition due to fog if the fog value is reasonably low.

The Density-Exposure Relation.—The relation between exposure and the response of the material, as shown by the density produced under given conditions of development, is usually presented in the form of a curve in which density is plotted against the logarithm of the exposure. Such a curve is shown in Fig. 240. As this method of expressing sensitometric data was developed by Hurter and Driffield, it is frequently referred to as the H and D curve; it is also termed the characteristic curve, or the D log E curve.

This curve may be divided into three parts, according to its slope or gradient: (1) The region of increasing gradient (toe), (2) the region of constant gradient (linear), and (3) the region of decreasing gradient. With greatly prolonged exposures, the descending curve results in a positive image rather than a negative. This region is known as the region of *reversal.*

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[19] Jones, *Photographic Sensitometry,* Eastman Kodak Co. 1935.

[20] Meidinger, *Z. physik. Chem.* **114** (1924) 89; Wilsey, *Phot. J.* **65** (1925) 454; Pritchard, *Phot. J.* **67** (1927) 447.

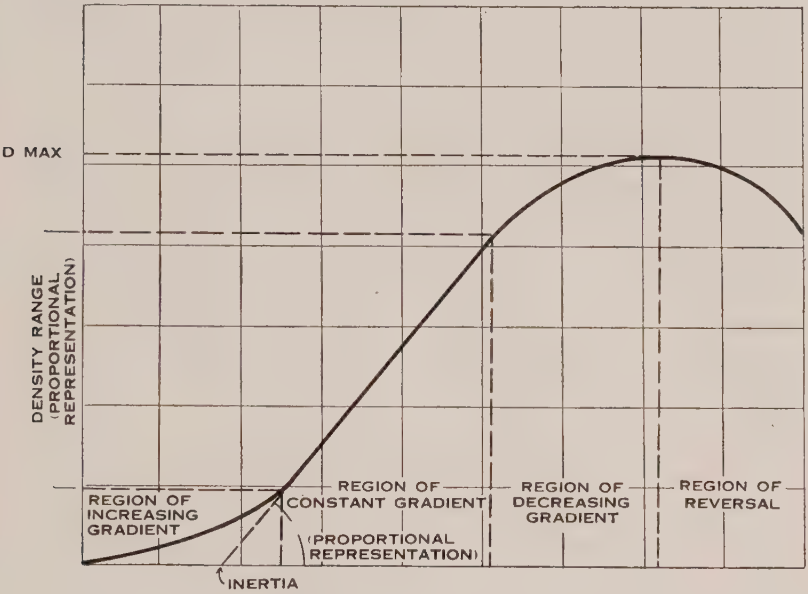

FIG. 240. The D log E Curve.

The region of constant gradient, or the straight-line portion of the curve, may also be defined as the *period of proportional representation.* Throughout this range of exposure, density is proportional to log exposure. Since density is proportional to log opacity (by definition) it is evident that the opacities within this range of exposures are proportional to the exposures which produced them. In other words, the opacities of the negative are proportional to the exposures produced by the corresponding brightnesses of the subject.[21]

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[21] The equation of this curve may be represented approximately as a chemical reaction of the first order

$$\gamma = \gamma_\infty \ (1 - e^{-kt})$$

where γ_∞ is the value of γ obtained if development is carried to completion, k the velocity constant of development, which depends on the developer and the temperature at which it is used, and t is the time of development for a given gamma.

The straight line is sometimes, following the terminology of H and D, referred to as the period of correct exposure. It would be well, however, if this designation be discontinued for if, as is the case in practice, the period of correct exposure be defined as that portion of the *D* log *E* curve which may be used to produce a *print* possessing satisfactory tone reproduction, then the range in exposure available extends considerably beyond the limits of the straight line portion of the curve.

There is no constant relationship between density and log *E* in either the region of increasing or decreasing gradient. In the former, the gradient and hence the density differences increase with log exposure; in the second case, the density differences decrease with log exposure (Fig. 240). The region of increasing gradient is frequently termed the period of underexposure. However, in view of the fact that a considerable portion of this region may be, and in practice is, used without producing results which are unsatisfactory from the standpoint of tone reproduction, this designation may be truthfully applied only to its lower extremity.

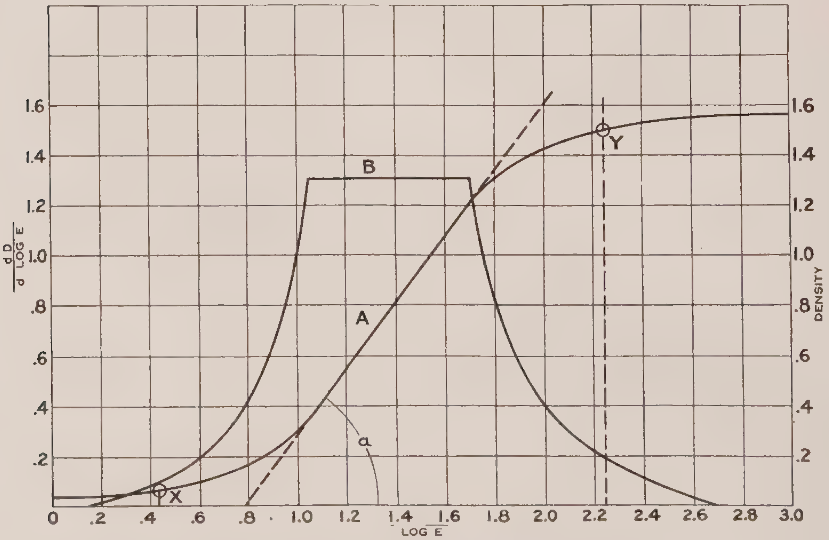

Fig. 241. The Gradient log *E* Curve.

Barber—Device for Plotting Characteristic Curves. J. Sci. Instr. **17** (1940) 95.

The period of reversal is reached only with greatly increased exposures on ordinary negative materials, and is without practical significance.

The Gradient Log *E* Curve.—For some purposes, the variation in the gradient, or slope, of the *D* log *E* curve with log *E* is more useful than the usual *D* log *E* curve.[22] A *D* log *E* curve with its first derivative, in which gradient is plotted against log *E,* is shown in Fig. 241. The data for this curve may be obtained in one of several ways. For example, the slope of the *D* log *E* curve at any particular point may be determined with fair precision by drawing a tangent to the curve at the point in question, and determining the slope, or gradient, of the tangent line. By repeating this procedure for a sufficient number of points, the necessary data may be obtained. A second method consists in taking a number of equally spaced points along the log *E* axis and calculating the density difference for each log *E* interval.[23]

Effect of the Degree of Development on the *D* Log *E* Curve.—Since, with increasing development, the densities increase proportionally, it is evident: (1) that the density *differences* increase with the time of

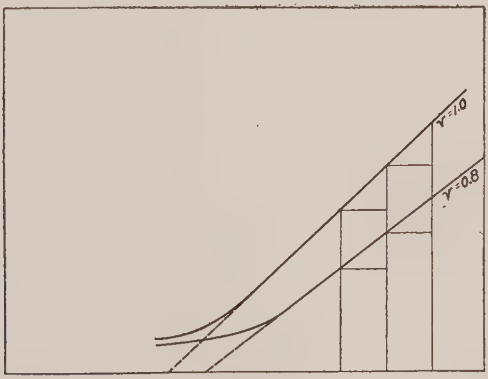

FIG. 242. Diagram Illustrating the Effect of the Time of Development on the density relations. The two *D* log *E* curves differ only in the time of development. The three perpendicular lines represent equal increases in exposure. The points of intersection of the three perpendiculars and the *D* log *E* curves represent the densities produced for the three exposures at the different times of development.

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[22] Renwick, *Phot. J.* **61** (1921) 10. Jones and Russell, *Phot. J.* **75** (1935) 657. Jones, *J. Franklin Inst.* **227** (1939) 297.

[23] For other methods of calculating gradient values, see: Renwick, *Phot. J.* **77** (1937) 6. Southworth, *Brit. J. Phot.* **85** (1938) 420. Turner, *Brit. J. Phot.* **85** (1938) 447.

development, while (2) the density *ratios* remain unchanged, and (3) the gradient, or slope, of the straight-line portion of the D log E curve increases. See Fig. 242. The slope of the straight line portion of the D log E curve, or the tangent of the angle between it and the log E axis, being indicative of the differences in density, is therefore also a measure of the degree of development or *gamma.*

Gamma is thus the ratio of the difference between any two densities on the straight-line portion of the D log E curve and the difference in the logarithms of the corresponding exposures, or

$$\gamma = \frac{D_2 - D_1}{\log E_2 - \log E_1}.$$

When gamma is equal to 1.0, the density differences are proportional to the differences in the logarithms of the exposures which lie within the straight-line portion of the D log E curve. In a camera exposure, these exposures are the direct result of differences in brightness; *hence* with development to a gamma of 1.0 the differences in density are proportional to the logarithm of the brightnesses of the corresponding parts of the subject. As density is the logarithm of the opacity, it follows that the ratio of the opacities is the same as that of the brightnesses which they represent. Development to a gamma of less than one results in the opacity differences being less than the brightness differences of

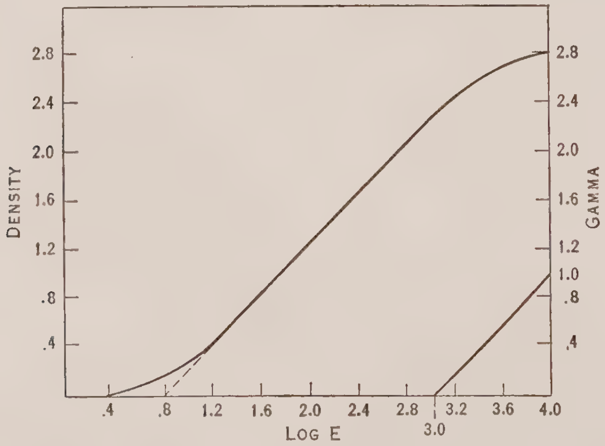

FIG. 243. Graphical Method of Calculating Gamma. (H and D Method.)

MENDELSSOHN—A New Gammeter. Phot. J. **79** (1939) 90.

the subject, while with development to a gamma greater than one, the opacity differences are also greater.

Calculation of Gamma.—To determine the value of gamma from the D log E curve using the formula

$$\gamma = \frac{D_2 - D_1}{\log E_2 - \log E_1}$$

erect two perpendiculars from the exposure axis to the points of intersection with the straight-line portion of the curve. Determine the densities at the points of intersection and substitute the density and log exposure values in the equation.

If, in Fig. 243, a line is drawn from the exposure axis at a log E value of 3.0 parallel to the straight line portion of the D log E curve, the angles of both with the exposure axis will obviously be equal since the lines are parallel. The tangents of the two angles are likewise equal and both are equal to gamma. Now, in the right angle triangle formed by the constructed line, the tangent of the angle is equal to the altitude divided by the base. The base, however, is equal to 1.0, since the difference in log units is 1.0. Consequently, if the right hand side of the chart is marked with a scale corresponding to the density scale on the left side, the point of intersection of the constructed line and the scale is equal to gamma.

In practice, gamma is usually determined by means of a transparent scale known as a *gammeter* (Fig. 244). If the arrow on the left side of the base line is placed on a point along the straight line portion of the D log E curve, with the base of the gammeter parallel to the log E axis, the point of intersection of the straight-line portion of the curve and the scale indicates the gamma.

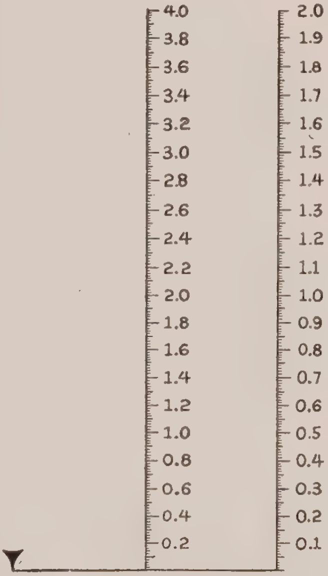

FIG. 244. Scales for the Determination of Gamma. (Gammeter.)

Gamma and Contrast.—The term, gamma, is frequently used as an expression of contrast. This is the case only under certain conditions. The contrast of a negative is determined by three factors:[24] (1) the contrast, or brightness range of the subject, (2) the exposure and (3) the degree of development, or gamma.

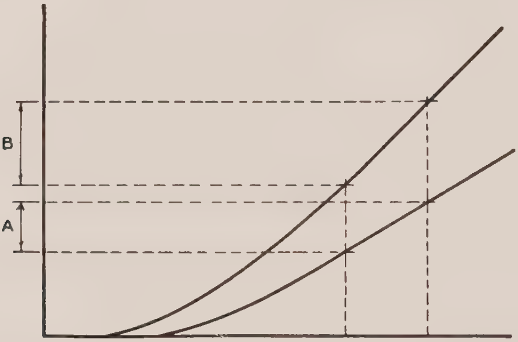

Fig. 245. Diagram Showing How the Density Range of the Negative is Increased by Development. If the vertical lines represent the minimum and maximum exposures, then *A* and *B* indicate the corresponding density range of the image for the *D* log *E* curves shown.

It is obvious that if a negative of a subject having a short brightness range, and another of a subject with an extended brightness range, are developed together, to the same gamma, the contrast of the second negative will be greater than the first.[25]

Exposure is without effect on negative contrast throughout the exposure range within the straight-line portion of the *D* log *E* curve, but if other portions are employed in the making of the negative, the contrast is reduced (Fig. 246).

Gamma represents *relative* contrast; i.e., relation of negative contrast, or opacity range, to subject contrast, or brightness range, but *only if the exposures are all within the period of proportional representation.*

The Time-Gamma Curve.—The relation between the time of development and gamma for a given photographic material, developer, and conditions of development can be determined by developing a number of sensitometer exposures for different times, determining the

[24] If the subject is in color, the color sensitivity of the emulsion must be considered.

[25] Negative contrast in this case is defined as the difference in the minimum and maximum densities (opacities) of the image.

Renwick—An Instrument for the Measurement of Gamma. Phot. J. **54** (1914) 163.
White—Gamma by Least Squares. J. Soc. Mot. Pict. Eng. **18** (1932) 584.

value of gamma for each time of development and plotting gamma against the time of development.

In Fig. 247, for example, are five *D* log *E* curves for a well-known film developed 2, 4, 6, 8 and 10 minutes. Plotting gamma against the corresponding times of development results in a *time-gamma curve* (Fig. 247). From this curve the time of development under the same conditions for any desired gamma is obtained by extending a line from the desired gamma, parallel with the time of development scale, to the point of intersection with the time-gamma curve. A line from this

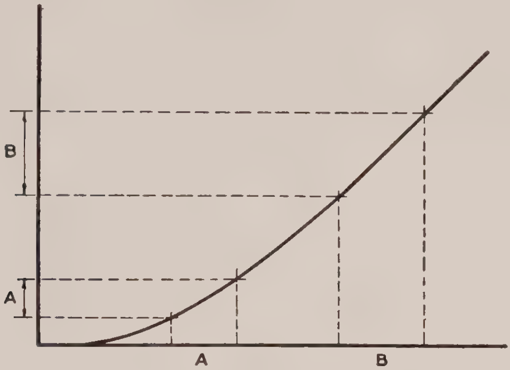

FIG. 246. Diagram Showing How the Density Range of the Negative Varies with the Exposure. The exposure range of *A* is the same as that of *B*, but the density range corresponding to *B* is greater than that of *A* because of the portion of the *D* log *E* curve employed.

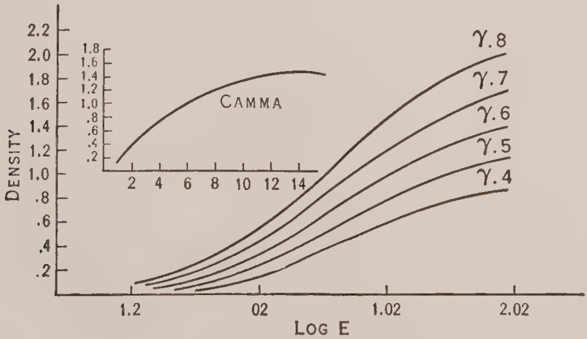

FIG. 247. *D* log *E* Curves Showing the Variation with Increasing Times of Development and the Time-gamma Curve (upper left) Obtained by Plotting Gamma as a Function of the Time of development.

point, perpendicular to the base, cuts the time of development scale at the corresponding time of development.

By reversing the procedure, the gamma produced by a given time of development may be found.

It should be noted, however, that these values are without practical significance unless the conditions of development are exactly duplicated. Values obtained, for instance, from tray development cannot be directly applied to tank development, nor can results obtained with a fresh developer at a given temperature be applied to a used developer, nor to another film.

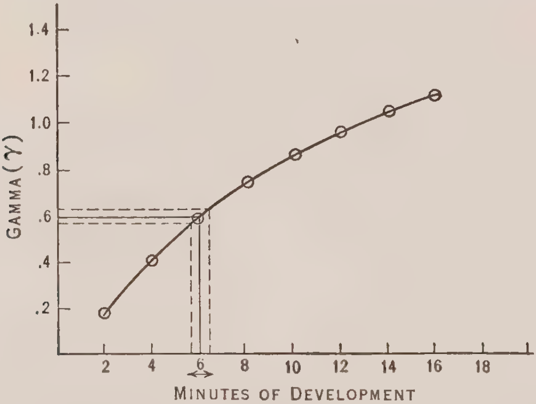

FIG. 248. Time-gamma Curve Showing How the Processing Latitude is Calculated.

The variation in the time of development possible for a given tolerance in gamma is termed the *processing latitude.* If, for example, a gamma of 0.5 must be maintained within a tolerance of plus or minus 0.04, the permissible variation in the time of development may be found by drawing lines from the two gamma values, namely 0.46 and 0.54 (Fig. 248), to their intersection with the time-gamma curve and dropping perpendiculars from these points of intersection to the time of development scale. For any given conditions of film and developer, the processing latitude increases with the degree of development, or gamma. Processing latitude is a very important characteristic when sensitive materials must be developed to certain prescribed gammas, as in the processing of motion picture sound records.

Gamma Infinity.—The highest gamma obtainable with any given material is termed *gamma infinity* (γ_∞). The value of gamma infinity depends chiefly upon the sensitive material,[26] and to a lesser degree upon the composition of the developer. Emulsions designed for portrait work have a low gamma infinity as a high degree of contrast is not required in portrait work, in fact, would be a disadvantage. In commercial, landscape and general exterior work, greater contrast is required and sensitive materials for these purposes attain higher values of gamma infinity than those made for portrait work. The greatest contrast of all is secured with emulsions of the process type as used for copying line work in black and white where absolutely clear lines together with a field of the greatest possible opacity are required. Typical values for maximum gamma:

High speed portrait film	1.3
High speed press film	1.8
Commercial panchromatic film	2.0
Fine grain panchromatic film	1.6
Process film	3.0
Photo litho film	5.0

Gamma infinity may be determined experimentally, but as it involves the measurement of very high densities which are affected by the fog, the process is subject to large experimental errors and gamma infinity is generally determined by calculation.

With two sensitometric strips, the time of development being in the ratio of 1:2

$$\gamma_\infty = \frac{(\gamma_2)^1}{(2\gamma_1) - \gamma_2}.$$

[26] Relation between γ_∞, γ and emulsion speed. The relation between γ_∞ and H and D speed was found by Southworth to be expressed by the equation

$$\log \gamma_\infty = \log a - b \log S$$

where a and b are constants for emulsions of the same type. Therefore,

$$\gamma_\infty = \frac{a}{S^b} = aS - b.$$

a and probably b is higher for panchromatic material. *Brit. J. Phot.* **84** (1937) 611.

Trivelli and Smith found that an exponential relationship holds not only for γ_∞ but for any fixed developing time. $\gamma S^b = a$. a increases and the exponent b decreases with increasing times of developments. *Brit. J. Phot.* **85** (1938) 307.

Mees and Sheppard—On the Highest Development Factor Obtainable on any Plate. Phot. J. **43** (1903) 199.

Renwick—An Improved Method of Computing the Velocity Constant and Gamma Infinity. Phot. J **63** (1923) 331.

Toy and Higson—Factors Determining Gamma Infinity. Phot. J. **63** (1923) 68.

The Measurement of Sensitivity or Speed.—The measurement of sensitivity, or speed, is a very important part of sensitometry; in fact, some methods of sensitometry are concerned wholly with the measurement of this characteristic. Four criteria have been used to measure the sensitivity of photographic materials:

1. *The exposure required to produce the least perceptible density.* (Threshold value.)
2. *The exposure required to produce a certain density.* (DIN and Weston methods.)
3. *The exposure obtained by the projection of the straight-line portion of the D-log E curve to the log E axis.* (The inertia of Hurter and Driffield.)
4. *The exposure at the point on the D-log E curve representing the minimum useful density difference.* (The minimum gradient method of Jones, Russell and others.)

Methods of Speed Determination Based on Threshold Values.—The threshold value may be defined as the exposure required to produce the first visible density under given viewing conditions as, for example, when the sensitometric test strip is placed emulsion side down on a sheet of white paper. The principal methods of speed determination based on threshold values are (1) the Scheiner, (2) the Eder-Hecht, (3) the Warnerke, and (4) the Chapman-Jones. The last two are of historical interest only and the second is limited to Germany and German speaking countries.

The best known method of measurement based upon threshold values is that due to Scheiner (1894). The Scheiner number was obtained originally by exposing the sensitive material in a rotating disk sensitometer, having an exposure range of 1 to 100 divided into 20 equal steps numbered from 1 to 20, developing under certain prescribed conditions, and expressing speed by the number of the step producing the threshold density. The ratio of exposures between consecutive

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Davis and Neeland—Experimental Study of Several Methods of Representing Photographic Sensitivity. Bur. Stand. J. Res. **7** (1931) 495.

Davis and Neeland—Methods of Denoting Sensitivity. J. Opt. Soc. Amer. **21** (1931) 416.

Formstecher—Proposals for a Practical Index of Speed. Phot. Ind. (1926) 1146.

Luther—Interpretation of the Characteristic Curve. Phot. J. **65** (1925) 185.

Thorne-Baker—Interpretation of the Characteristic Curve. Phot. J. **65** (1925) 181.

steps on the Scheiner sensitometer is as 1 : 1.27; hence, the relative speed as represented by any given Scheiner number is 1.27 greater than the next lower.

In time, various modifications were made in the original method so that no reliance could be placed in the Scheiner speed number and in 1931 it was officially superseded in Germany, the land of its origin, by the DIN method.

The Eder-Hecht method employs a special sensitometer tablet in which the density increases continuously rather than in steps. Lines are ruled across the tablet and numbered so that after the sensitive material has been exposed either to the light of a lamp burning amyl acetate or to burning magnesium, developed and laid emulsion side in contact with white paper, the highest number visible is taken as a measure of the speed of the sensitive material.

The Warnerke sensitometer consisted of an exposure tablet containing 25 numbered squares of pigmented gelatin, each having a density one-third greater than the preceding, so that an increase of three numbers on the tablet represented a decrease in light intensity of 50%. The plate to be tested was exposed behind this tablet to the light from a phosphorescent tablet which formed a part of the apparatus. The speed of the sensitive material was expressed in terms of the highest number which could be read, the number on the image being in white on a faint gray square.

The Chapman Jones method was essentially the same as the Warnerke except for minor differences in the step tablet and the substitution of a standard candle for the phosphorescent tablet of Warnerke.

There are several objections to the use of the threshold exposure as a means of evaluating the speed of a sensitive material. In the first place, the threshold exposure is not a constant, but depends upon the conditions under which the developed sensitometer strip is examined and the conditions of development.[27]

Much more serious, however, is the fact that the threshold exposure is not a true index of the speed of a photographic material. From the standpoint of practice, the speed of a sensitive material is measured, not by the exposure required to produce a trace of an image, but by that required to produce an image whose density differences more or less satisfactorily represent the brightness differences of the subject photographed. As there is no fixed relationship between the threshold exposure and that required for satisfactory rendering of the gradations of the subject, the threshold exposure is not an adequate means of measuring the effective speed of a photographic material.

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[27] Bullock, *Sci. et Ind. Phot.* (1926) 33; (1927) 5; (1929) 24.

Methods of Speed Determination (Based Upon the Exposure Producing a Given Density—Other than Threshold Density).—In some fields of applied photography where the reproduction of tone differences by the sensitive material is not involved, as for example, in spectrography and astronomy, the exposure required to produce the necessary density with given conditions of development is an adequate measure of the practical speed of the film or plate. In the mapping of stellar spectra, for example, a density of 0.6 is adequate for the detection and measurement of the absorption lines. The sensitivity of a film or plate under such conditions would be inversely proportional to the exposure in meter-candle seconds to light of the accepted color temperature which will produce a density of 0.6 when developed to a standard gamma in a particular developer.

Obviously speed values determined in this manner are open to the same objections as the threshold value, where the reproduction of brightness differences by the photographic material is the primary consideration in the evaluation of its effective speed.

The principal method of speed determination based upon the exposure required to produce a particular density, which is above the threshold density, is the Deutsche Industrial Normal, or DIN System, in which a density 0.1 greater than the fog density is used and the Weston numbers which are derived from the exposure producing a density equal to gamma.

In 1931, the manufacturers of photographic materials in Germany adopted a method of determining speed which is termed the DIN method; the letters DIN being "Deutsche Industrie Norm," or German Industrial Standard.

In this method, the sensitive material is exposed in a special sensitometer employing an intensity scale of thirty steps, ranging in density from 0 to 3.0, the density increment of each step being 0.1. The light source is a standardized 40 watt incandescent lamp which is used with a filter to produce a daylight standard. The exposure of 1/20 second is made by means of a drop shutter.

After exposure, the sensitometer strip is developed in a specified metol-hydroquinone developer. In view of the fact that there is no prescribed time of development, the time for any particular sensitive material is determined after preliminary tests have revealed the development time which results in optimum rendering of the lower densities.

The speed of the material is determined from the step having a density of 0.1 greater than fog, rather than the lowest perceptible density as in the threshold method. This particular step is found by measuring the densities in a special comparison densitometer in which one of the comparison beams passes through the fog strip and the other, the exposed portion of the sensitometric strip. A supplementary density of 0.1 is placed in the comparison beam which passes through the fog density so that it is increased automatically by 0.1. When the photometric field is uniformly illuminated, the density of the exposed area is thus 0.1 greater than fog. The density of the corresponding step on the sensitometer step wedge is then determined. This density multiplied by 10 constitutes the DIN speed.

DIN speed numbers are, therefore, inversely proportional to the common logarithm of the required exposure, and an increase of three units in the speed number is equivalent to a speed ratio of 1 : 2.

The DIN method has been rather seriously criticized in other countries, particularly the specifications relating to development. These, it is argued, are not comparable to those employed in practice. The specifications for development result, with some materials, in a degree of development in excess of that which would be given in practice. This would not be a serious matter if the ratio of the speed for the so-termed "Optimum Development" to that at normal development were the same for all materials. Experimental evidence available at the present time indicates that there is a fairly constant ratio for ordinary roll film, but that considerable variation exists with other types of sensitive material. In this case, it would be possible for two materials having the same DIN speed number to show considerable differences in effective speed when developed to the same degree of contrast. However, it is not possible to express the speed in terms of contrast (or gamma) since there are certain sensitive materials which increase considerably in speed as development progresses, but, beyond a certain point, show only slight increase in contrast.[28]

[28] Ferguson, *Brit. J. Phot.* **81** (1934) 380; "International Standardization of Speed Numbers," *Brit. J. Phot.* **82** (1935) 483; Jones, *Photographic Sensitometry,* p. 63; Jacobsen, *American Annual of Photography,* 1937; Clark, *American Annual of Photography,* 1937.

HANSEN—Relation between Scheiner and DIN Sensitivities. Brit. J. Phot. **82** (1935) 131.

BILTZ AND EGGERT—Connection between DIN and Scheiner Values. Phot. Ind. **32** (1934) 1296.

LUTHER—The Sensitometric Method "DIN 4512." Proc. Ninth Int. Congress of Phot. Paris, 1935. Sci. et Ind. Phot. (II) **6** (1935) 260.

Weston Speeds.—Weston speeds are designed primarily for use with the Weston exposure meter and are designed to indicate not so much the minimum exposure which will produce a satisfactory negative, but an exposure which will provide the greatest tolerance in exposure to compensate for variations in shutter speed, color of subject, color of light and other factors which affect exposure. The Weston speeds published are based upon tests of films and plates on the market made periodically in the sensitometric laboratories of the Company.

The exposures are made on an Eastman Sensitometer, type IIb (see Page 396) and developed in the formula recommended by the manufacturer to stated gammas. The D log E curve is then plotted and the Weston speed determined from the formula

$$\text{Speed} = \frac{4}{E},$$

where E is the exposure for a density $= \gamma$.

H and D Speeds.—When the straight line portion of the characteristic curve is extended to intersect the log E base, an exposure is indicated which was termed by Hurter and Driffield the *inertia*. The inertia is an inverse measure of speed so that a material of high speed has a low inertia and vice-versa. It is necessary, therefore, to take the reciprocal of the inertia in order to obtain numbers which are directly proportional to the speed of the sensitive material. However, since the reciprocal of the inertia is in some cases less than unity, it is customary to multiply the reciprocal by a constant so as to obtain more convenient numbers. Present American practice is to multiply the reciprocal value by 10. The H and D speed in this case is represented by

$$S = \frac{10}{\text{Inertia}}.$$

Hurter and Driffield used a factor of 34 and still other values have been employed.[29]

The inertia was selected by Hurter and Driffield as a means of expressing speed because, with the photographic materials then available (1890), it was a characteristic of the material which was not affected by variation in the time of development (provided the developing solution does not contain a soluble bromide); the developing agent (except for a few agents of low reduction potential); or the composition of the

[29] For the origin of the factor of 34, see Ferguson, *Phot. J.* **66** (1926) 514.

developing solution. If a bromide is added to the developer, or if the emulsion contains free bromide (the vast majority of negative emulsions now contain free bromide), the inertia is not constant for different times of development, but shifts to the left as the degree of development of gamma increases (Fig. 208). It is obvious that under these conditions, the speed of the material, as determined from the inertia, varies with the degree of development and that for each time of development, or gamma, there is a corresponding H and D speed.

Still other complications arise in expressing the speed of photographic materials by the inertia. In some cases, the material does not produce a satisfactory straight-line relationship between density and log exposure, or there may be two more or less well defined straight-line portions. In such cases, it is difficult to find the true inertia. There is likewise a wide divergence in the shape and position of the curve with different times of development, especially among materials of high sensitivity.

Finally speed, as determined from the inertia, ignores the toe portion of the *D* log *E* curve. However, the development of photographic materials, with an extended toe portion, has brought about the very general use of some of this portion of the curve in practical photography. Experience has shown that, within certain limits, it is possible to do this and still obtain acceptable, if not strictly accurate, tone reproduction. Under such conditions, the inertia does not represent the effective speed of the material.

Methods of Determining Speed Based Upon the Limiting Gradient.—The scientific investigator and the practical photographer do not regard the problem of measuring and expressing numerically the sensitivity of a photographic material from the same point of view. The former is concerned with the means of determining and expressing sensitivity from the relation between the radiant energy incident on the photographic material and its response to that energy after development. The practical photographer, on the other hand, evaluates sensitivity in terms of the exposure required to produce a negative from which, after having been properly developed, a satisfactory print can be made on his chosen paper. By a satisfactory print is meant one

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Baker—Interpretation of the Characteristic Curve. Phot. J. **65** (1925) 181.

Bloch—Interpretation of Results. Phot. J. **65** (1925) 186.

Davis and Neeland—Variation of Photographic Sensitivity with Development Time. J. Soc. Mot. Pict. Eng. **18** (1932) 742.

in which the brightness differences constituting the image form a satisfactory reproduction of the subject represented. In other words, the speed of a photographic material, from the standpoint of the practicing photographer, is determined by the exposure required to reproduce the brightness differences of the subject, by differences in negative density which will result in a satisfactory rendering of the subject *in the print.* From which it should be evident that any relationship between exposure and a particular density is unimportant; it is the exposure required to reproduce brightness differences which is important and this information is obtainable only from the slope, or gradient, of the D log E curve.

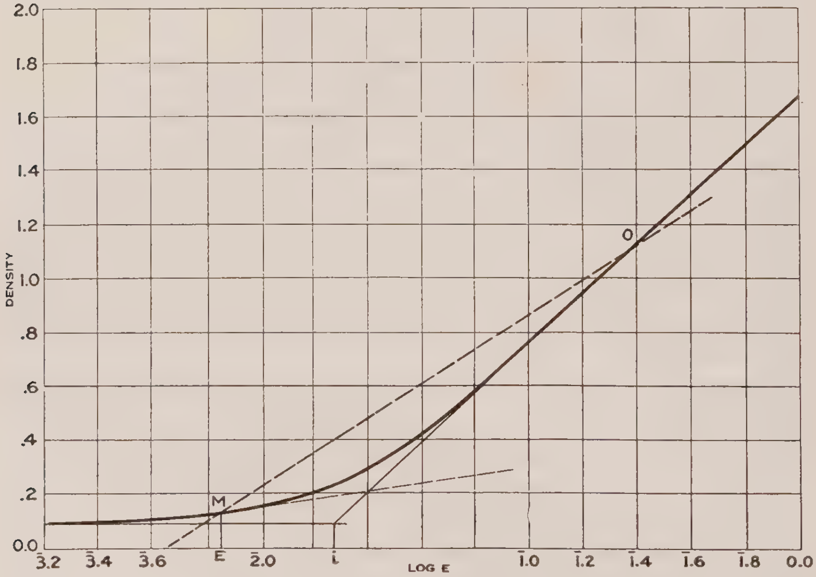

FIG. 249. Determination of Sensitivity from the Minimum Useful Gradient (Kodak Method). The gradient of the D log E curve at M is 0.3 of the average gradient between M and O representing a log exposure range of 1.5.

The point on the D log E curve at which the density differences, or the gradient, is just sufficient to produce satisfactory tone reproduction *in the print* is the *limiting,* or *the minimum useful, negative gradient.*

Methods of arriving at a measure of speed, or sensitivity from the exposure required to produce some particular gradient, have been discussed and advocated for several years[30] and the Eastman Kodak Company has since 1939 published speed values for its negative materials based upon a method developed in its laboratories for measuring effective camera speed in terms of the limiting gradient.[31]

The Kodak Limiting Gradient Method.—Sensitivity, as expressed by the Kodak limiting gradient method, is defined as *the reciprocal of the exposure at that point on the D log E curve at which the gradient is equal to 0.3 of the average gradient for a log exposure range of 1.5.* (Fig. 249.)

This method of determining speed was developed from a correlation of the sensitometric characteristics of a number of typical negative materials and the camera exposures required to produce a satisfactory print. This last was determined statistically. A series of test negatives were made, with accurately measured exposures, of a positive transparency having a brightness range of 1 : 30 which was regarded as approximating that of the average subject. An accurate intensity scale was placed alongside the positive transparency. The exposures for this series of test negatives varied from extreme underexposure to a very full exposure. These negatives were developed to the recommended gammas and printed on the paper producing the best results. Finally, the prints were studied carefully by 200 selected examiners, who classified the prints as (1) bad, (2) acceptable, (3) excellent reproduction of the original subject. The minimum negative exposure producing prints which were rated excellent by the majority of the examiners was taken as an indication of the effective speed of that particular sensitive material. This exposure, when located on the *D* log *E* curve of the sensitive material, was found to correspond with the exposure at which the gradient is 3/10 of the average gradient for a log exposure range of 1.5 (brightness range 1 : 30).[32]

Determination of the Limiting Gradient.—The determination of the abscissa of a point on the characteristic curve at which the gradient is a specified fraction of an average slope may, of course, be made without the aid of instruments other than the standard instruments of sensitometry. Given the characteristic curve *A* in Fig. 250, a gradient, or first derivative, curve, *B*, is plotted. A point, *a*, is selected on the *D* log *E* curve and *a′* established so that log $Ea' - Ea =$ 1.50. The slope of this line, which is the average gradient of the curve between *a′* and *a*, is then plotted on the gradient scale at the left of the chart. The gradients of *b*, *b′*; *c*, *c′*; etc. are determined and plotted and curve *C* drawn through the plotted points. Curve *C* is therefore the average gradient for log *E* intervals of 1.50 plotted against the minimum log *E* value of each interval. The ordinates of curve *B* are then multiplied by $1/K$, *K* being the detail compression factor (0.30) and plotted on the same scale to obtain curve *D*. A perpendicular from the intersection point of curves *C* and *D* to curve *A* locates the point on the *D* log *E* curve at which the gradient is 0.3 of the average for a log *E* range of 1.50.

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[30] Luther, *Phot. J.* **49** (1925) 185. Jones and Russell, *J. Opt. Soc. Amer.* **25** (1935) 396. Luther, *Sci. et Ind. Phot.* **4** (1924) 1. Lapeyre, *Bull. Soc. franç.* (3) **16** (1929) 10, 28. Romer, *Sci. et Ind. Phot.* (2) **7** (1936) 117.

[31] Jones, *J. Franklin Inst.* **227** (1939) 297, 497.

[32] For a critical comparison of this and other methods of expressing the speed of negative materials, see Jones and Nelson, *J. Opt. Soc. Amer.* **30** (1940) 93.

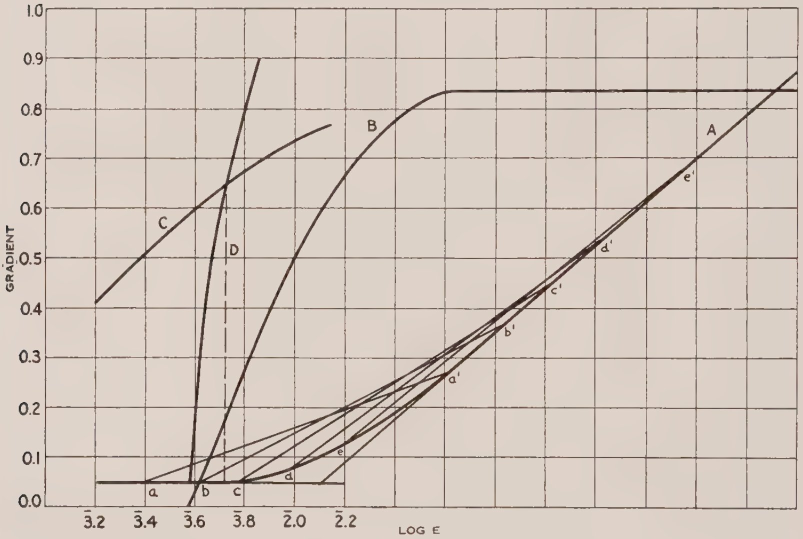

FIG. 250. Method of Determining the Point of the *D* log *E* Curve at which the Gradient is a Specified Fraction of the Average Gradient.

The drawing of the curves *B* and *C* is a rather laborious process and a very useful shortcut is provided by the semi-automatic gradient ratio-reading device which has been developed by Mr. C. N. Nelson of the Kodak Laboratories.

This gradient speed meter is composed of two parts as shown in Fig. 251. Part I is a rectangular transparent plastic sheet upon which are inscribed two parallel lines *CD* and *EF*. These lines are separated by a distance which is equivalent to a log *E* value of 1.5 on the characteristic curve which is to be analyzed. Part I also carries a small round hole at *P* which marks the pivot point for a transparent movable arm in Part II. *P* is located 0.4 log *E* from *CD*. The arm has inscribed on it the straight line *AB* and the curved line *GH*, and it is punched with the hole *P*. The point *G* is spaced 1.9 in log *E* units from the point *P* as shown in Fig. 251. The shape and position of the curve *GH* on the movable arm is completely determined by the position of the pivot point *P* and by the requirement that the minimum gradient which is the slope of the line *AB* must be equal to 0.3 times average gradient. The curve *GH* theoretically extends to infinity. The analytical expression defining it is complicated and of no practical use. However, over its normal working range, *GH* is to a very high degree

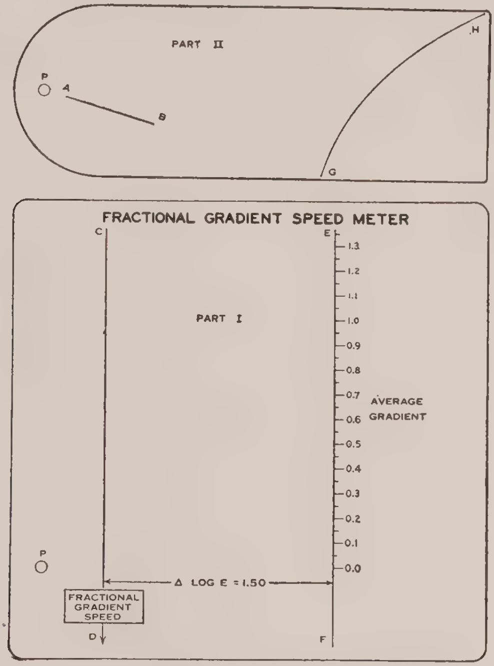

Fig. 251. Fractional Gradient Reader.

of accuracy the arc of a circle having a radius of 1.6 in density or log *E* units. When the device is assembled, Part II is fastened to Part I by a rivet through the hole *P* and is free to rotate about this point.

In use, the meter is placed on the H and D graph with the lines *CD* and *EF* parallel to the density axis. (See Fig. 251.) The meter is set with respect to the graph to a position at which the lines *EF*, *GH* and the *H* and *D* curve intersect at a common point while simultaneously the lines *AB* and *CD* intersect at another point on the toe of the curve. The meter parts are kept in an orientation such that these lines always intersect, while the device as a whole is slid along the characteristic curve. At some point on the curve, it will be noted that the line *AB* becomes tangent to the characteristic curve.

The characteristic curve at the point of tangency then has a gradient which is equal to 0.3 times the average gradient over the 1.5 log *E* interval. The point of tangency can usually be located after two or three trials requiring only a few seconds, and the speed of the emulsion, is, of course, quickly determined by the abscissa value of this point.[33, 34]

Latitude.—The range of exposure within which the gradient of the *D* log *E* curve is constant, that is the straight-line portion is also termed the *latitude* of a sensitive material.

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[33] This method, together with direct visual photometric methods, is described in a paper by Clifton Tuttle, *J. Opt. Soc. Amer.* **29** (1939) 267.

[34] The committee on standardization in the field of photography, American Standards Association, has recommended that speed be determined from the exposure at which the gradient on the *D* log *E* curve is 0.3 of the average gradient for a log *E* range of 1.5, *this average gradient being 0.7 in the case of roll film and film packs, and 0.6 with 35 mm. and other miniature camera films. J. Opt. Soc. Amer.* **31** (1941) 87.

JONES—Photographic Film Speeds as Evaluated in Terms of Print Quality. Brit. J. Phot. **87** (1940) 206, 217, 228, 241, 251, 263.

JONES AND NELSON—A Study of Various Sensitometric Criteria of Negative Film Speeds. J. Opt. Soc. Amer. **30** (1940) 93; Phot. J. **80** (1940) 152.

JONES AND RUSSELL—Minimum Useful Gradient as a Criterion of Speed. Ninth Int. Congress of Phot., Paris, 1935. Sci. et Ind. Phot. (II) **6** (1935) 325. Phot. J. **75** (1935) 657.

JONES AND RUSSELL—Minimum Useful Gradient as a Criterion of Photographic Speed. Phot. J. **75** (1935) 657.

ROMER, MARKOCKI AND BIERNAT—Numerical Expression of Speed Based on Relative Minimum Gradients. Proc. Ninth Int. Congress of Phot. Paris 1935. Sci. et Ind. Phot. (II) **6** (1935) 265.

MENDELSSOHN—The Recognition of Detail in the Negative. Phot. Korr. **73** (1937) 166.

The latitude of a sensitive material, which should not be confused with latitude in exposure, is defined as the difference in exposure units over which correct proportional representation is obtained, i.e., the straight-line portion of the D log E curve.

The latitude of a sensitive material is not a constant of the emulsion but varies with the degree of development, or gamma. As the latter increases, the projection of the straight-line portion of the D log E curve on the exposure axis decreases (Fig. 252) and consequently the latitude becomes less. Likewise, sensitive materials normally used at a high gamma, such as positive or process films, have a short exposure scale, or latitude.

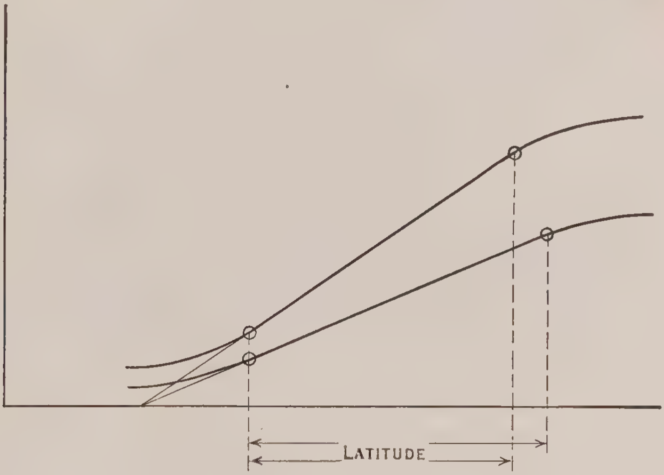

FIG. 252. D log E Curves Showing How Latitude Decreases with Gamma.

The *useful exposure range* of a sensitive material is usually greater than its latitude, as, generally speaking, it is possible to use portions of the curve at both extremities of the straight line portion without loss of quality in tone reproduction.

The useful exposure range is a very important characteristic of a photographic material, as it indicates the range of brightnesses which can be acceptably recorded in the negative and hence, in a large measure, the purposes for which the film or plate is suitable. Fortunately, it is greater than the range of brightnesses in the vast majority of the subjects photographed. Exceptions, of course, occur, but in general the range of brightnesses in ordinary subjects is about 1–30, or less, and only in exceptional cases does it exceed 1–100, while the exposure scale of a good negative material is usually not less than 1–200 and is frequently considerably more. The exposure scale of positive materials is much less and in general the higher the gamma to which the material is ordinarily developed, the lower is its latitude.

The greater the useful exposure range of a sensitive material, the greater is its *tolerance in exposure.* For any given photographic material, the greater the range of brightnesses in the subject, the less the tolerance in exposure.

Sensitometry of Photographic Printing Papers

The sensitometric methods employed in determining the characteristics of photographic printing papers are, in general, similar to those used in the study of negative materials. There are, however, some rather important differences. Owing to the failure of the reciprocity law, sensitometers employing an intensity scale are much to be preferred to time-scale instruments.[35] Indeed the use of sensitometers of the type commonly employed for negative materials can lead to results which are not in any way comparable with those obtained in practice in which positive materials are invariably exposed to an intensity scale. Furthermore, since the exposure range of papers is less than that of most negative materials, the exposure difference for successive steps should be less than in an instrument designed for use with negative materials. The exposure increment of sensitometers designed for papers should not exceed $\sqrt{2}$, while an exposure difference of $\sqrt[3]{2}$ is preferable. The light source should be of sufficient intensity to permit of exposures of the same order as those commonly applying to the practical usage of the material being investigated.

In the case of papers obviously, it is the light reflectance of the silver deposit (the *reflection density*) rather than the light transmitted (*transmission density*) which is of importance. Measurements of the amount of light reflected from a density are made in specially designed densitometers in which the area to be measured is illuminated by diffuse light so that any specular reflection is thrown to one side and only the diffusely reflected light is included in the measurements. The instrument shown in Fig. 253 is suitable for the measurement of the reflection densities of a paper as well as the transmission densities of a negative. The use of densitometers employing polarization for the measurement of reflection densities is open to question, since the light reflected from the paper may, under certain conditions, be polarized and this would lead to serious errors in measurement.[36]

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[35] An intensity scale sensitometer, employing a stepped diagram and a cylindrical lens, for the exposing of printing papers, has been described by Jones and Morrison, *J. Franklin Inst.* **228** (1939) 445, 605, 755.

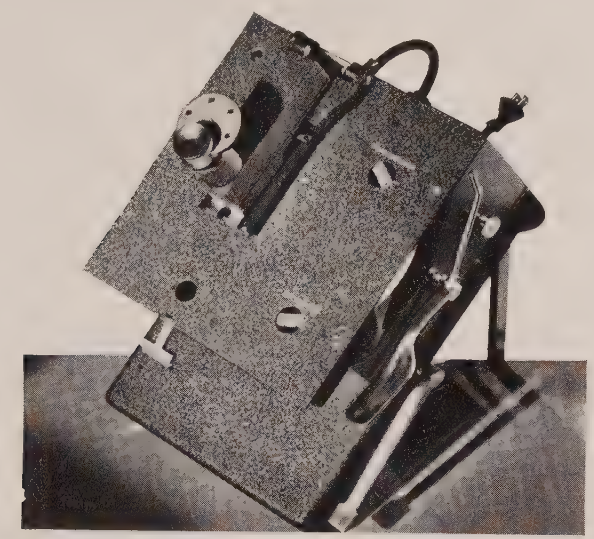

FIG. 253. Eastman Reflection and Transmission Densitometer.

The reflection density, unlike the transmission density, is not directly proportional to the mass of silver per unit of area, but depends upon (1) the surface reflection, (2) the reflectance of the paper stock and (3) the mass of silver. It may be expressed as

$$Dr = \log \frac{I}{R},$$

where I is the intensity of the light reflected from the paper base free of an image, i.e., fixed out without exposure or development, and R the intensity of light reflected from the deposit after a given exposure and development.

The *D* Log *E* Curve of Developing-Out Papers.—When a developing paper is exposed in a suitable sensitometer, developed and the

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[36] A modified form of the Bechstein illuminometer, designed especially for measuring paper densities, has been described by Jones and Morrison, *J. Franklin Inst.* **228** (1939) 445, 605, 755.

JONES AND MORRISON—Sensitometry of Photographic Papers. J. Franklin Inst. **228** (1939) 445, 605, 755.
URBACH—Studies on the Characteristic Curve of Photographic Papers. J. Opt. Soc. Amer. **31** (1941) 581.

reflection densities plotted against the logarithm of the exposures, the D log E curve is found to be similar to that of negative materials (Fig. 254). There are, however, some differences of importance. The portion of the curve approximating a straight line is less, the gradient or slope of this portion of the curve is, in general, quite steep, the exposure range also is relatively short and the maximum density is comparatively low. This is due to the fact that with papers we are dealing with a smaller mass of silver and that there are three surfaces from which the light is reflected: (1) the gelatin surface, (2) the silver deposit and (3) the paper base beneath the silver deposit. The maximum density, therefore, is limited by the amount of light reflected from the surface and is seldom greater than 1.5 to 1.8, even on glossy papers. On matt papers, it is much less, ranging from 1.1 to 1.3 (Fig. 254).

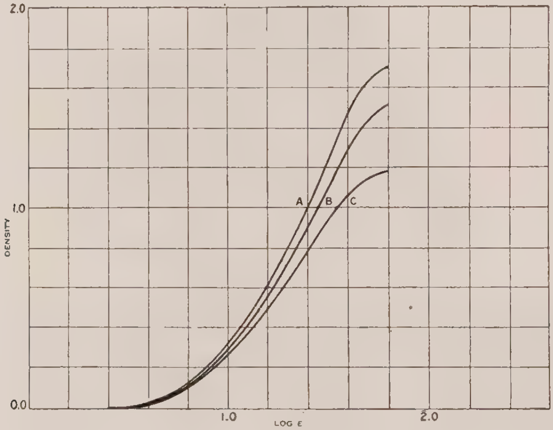

FIG. 254. D log E Curves of a Silver Chloride Contact Paper on (A) Glossy Paper (B) Semi-matt Paper and (C) Matt Paper, Showing Effect of Paper Surface on Maximum Density and Density Range.

The difference in the amount of light reflected from the base of the paper and that reflected from the maximum black which the emulsion will produce, constitutes the *brightness range* of the paper. Since $D = \log I/R$ the density range is the logarithm of the brightness range.

Effect of Variation in the Time of Development on the D Log E Curve of a Photographic Paper.—As with negative materials, the shape of the curve depends partly upon the developing time. In Fig. 255 [37] are shown characteristic curves for a typical silver chloride contact printing paper for developing times ranging from 16 to 280 seconds. It will be observed that the increase in the gradient of the straight-line portion (gamma) with increased development is slight and that, except for the very shortest developing time, the principal result of extending development is to shift the entire curve towards the left. Chloro-bromide and bromide papers behave somewhat differently (Fig.

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[37] Jones and Morrison, *J. Franklin Inst.* 228 (1939) 445, 605, 755.

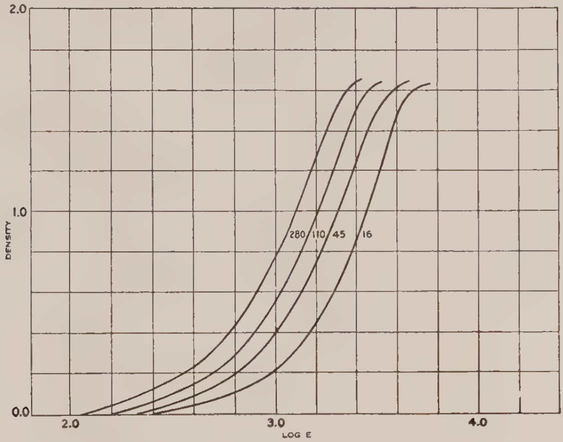

FIG. 255. *D* log *E* Curves Showing Change in the Shape of the Curve with Developing Time for a Silver Chloride Contact Paper.

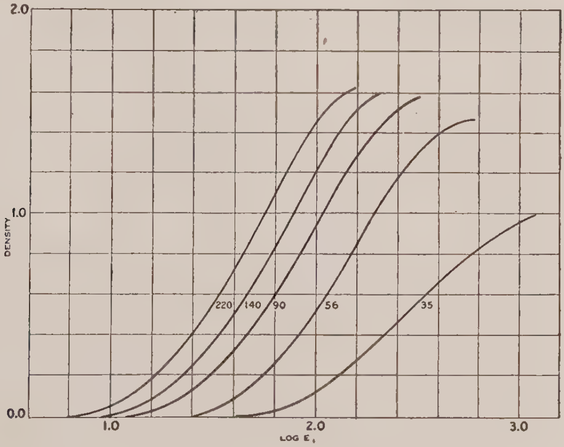

FIG. 256. *D* log *E* Curves Showing Change in Shape of the Curve with Developing Time for a Chlorobromide Paper.

256), the last mentioned more closely resembling a negative emulsion in its behavior. With developing papers, it is necessary to develop to the point at which a stable curve shape is reached, if the maximum density, i.e., a good black, combined with good reproduction and good print quality is to be obtained; hence the contrast of the image cannot be controlled by varying the time of development as in the case of negative materials.

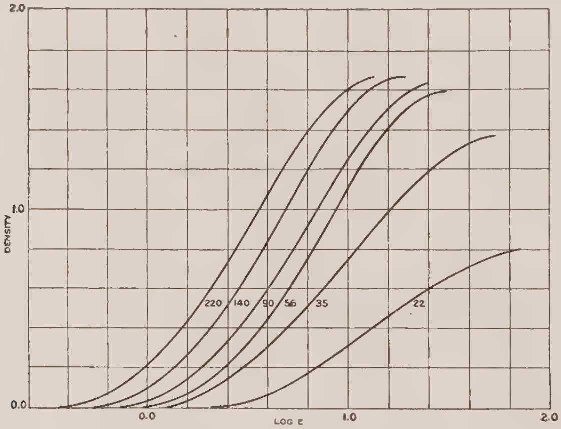

FIG. 257. *D* log *E* Curves Showing the Change in the Shape of the Curve with Developing Time for a Silver Bromide Paper.

Contrast of Printing Paper.—Developing papers accordingly are usually manufactured in several grades differing in "contrast," i.e., in the contrast of the print produced from a given negative. In Fig. 258 are shown the *D* log *E* curves of the six grades of a silver chloride, contact paper, all developed to the point at which a stabilized curve shape is obtained. (See note 37.) The curves for the different grades have been shifted laterally along the exposure axis to avoid the overlapping and possible confusion which might arise if all were plotted on the same exposure scale. It will be observed that the maximum density and, hence, the brightness range is practically the same for all six grades, also that the straight line portion, or the portion approximating a straight line is relatively short. It will be noted also that the slope, or gradient, of the curve increases steadily from grade 0 to grade 5; also that the exposure range, i.e., the range of exposures required to produce the range of densities available on the paper, becomes less and less as the gradient of the curve increases. Thus, the gradient of the *D* log *E* curve of a printing paper increases, and the exposure range becomes less, with the contrast. The contrast of a printing paper, however, is not wholly a function of the gradient, but depends also upon the maximum density. Thus, of two papers having the same gradient characteristics, that having the greater maximum density, i.e., the greater the density or brightness range, will have the greater available contrast. Thus, the contrast of a printing paper depends upon the gradient characteristics of the *D* log *E* curve, namely *dD/d* log *E* and the density range.

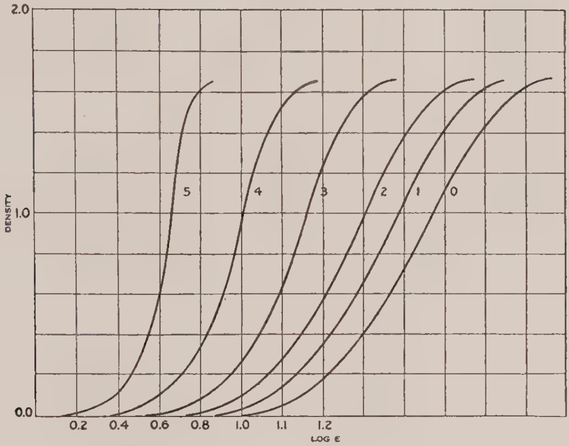

FIG. 258. *D* log *E* Curves Showing Change in Curve Shape for Different Contrast Grades of a Silver Chloride Contact Paper.

According to Jones, the contrast (Ω) of a photographic printing paper is expressed

$$\Omega = \frac{(D \max - D \min)\cdot[\bar{G}(D)]}{I\Delta D^2},$$

where $G(D)$ is the average gradient in terms of equal density increments on the *D* log *E* curve, and $I\Delta D$ is the smallest density difference which the eye can distinguish under average print viewing conditions, i.e., approximately 0.007.[38]

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[38] Jones, *J. Franklin Inst.* **202** (1926) 177; **203** (1927) 111; **204** (1927) 41. Reference should also be made to Bontenbal, *Phot. J.* **78** (1938) 76 (with bibliography).

"A graphic method of evaluating contrast according to the formula just given is illustrated in Fig. 259. The curve *A* is obtained by plotting values of $dD/d \log E$ as a function of the corresponding density, not log exposure. A measurement of the area enclosed by the curve *A*

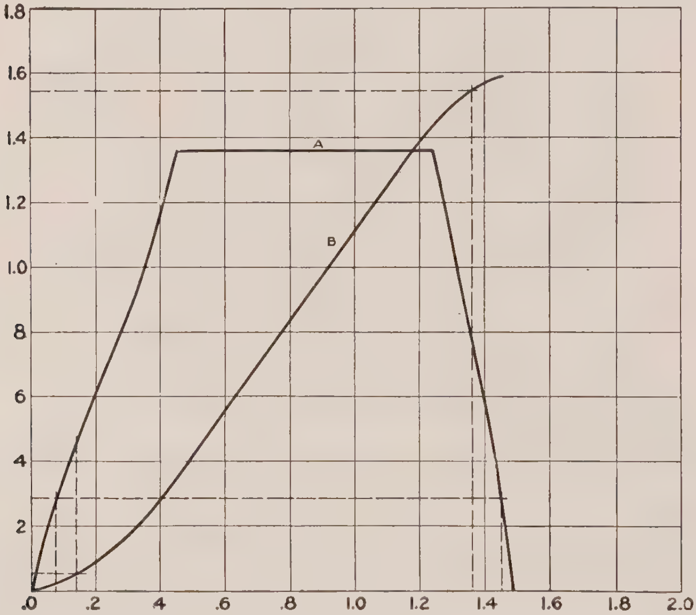

Fig. 259. Graphical Method of Determining the Contrast of a Printing Paper.

and the density axis now gives directly an evaluation of the contrast equation. It is only necessary to choose proper units for plotting this curve and to make the proper setting of a planimeter in order to obtain directly the desired value."[39]

Sensitometric Characteristics of a Typical Silver Chloride, Contact Printing Paper.—The following table, from measurements by Jones and Morrison, indicates the sensitometric characteristics of a typical silver chloride contact printing paper in terms of the log exposure range, maximum density, maximum gradient and contrast capacity, as determined in accordance with the formula in the preceding section.

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[39] Jones and Morrison, *J. Franklin Inst.* **228** (1939) 755. See also, Morrison, *Brit. J. Phot.* **89** (1940) 335.

Maximum Density

Contrast Grade	*S*	*ES*	*Log ES*	*1.7*		*1.53*		*1.4*		*1.3*	
				C, F		*B, E, G, K, X, Y*		*AA, P*		*A, H, Q*	
0	80	30	1.48	42	1.80	34	1.70	28	1.60		
1	75	26	1.41	50	1.90	40	1.80	34	1.65	29	1.30
2	50	20	1.30	60	2.45	49	2.10	41	1.90	34	1.70
3	40	15	1.18	72	3.20	59	2.70	49	2.40	41	2.10
4	20	9	0.95	87	4.10	70	3.50	59	3.20		
5	12	5	0.70	115	5.30	92	4.50	75	4.00		

The surface designations of the various papers as shown at the top are as follows:

A—Smooth, white matt.
AA—Smooth, lustre, cream white.
B—Smooth, semi-matt.
C—Smooth, glossy, pense.
E—Smooth, semi-matt, white.
F—Smooth, glossy, white.
G—Fine grain, lustre, white.
H—Fine grain, matt, white.
K—Smooth, semi-matt, cream.
P—Fine grain, lustre, ivory.
Q—Fine grain, matt, ivory.
X—Silk, semi-matt, ivory.
Y—Silk, semi-matt, cream.

Spectral Sensitivity.—The variation in the response of a photographic material with the wave length of the radiation to which it is exposed constitutes what is termed *spectral sensitivity* or frequently *color sensitivity.* The spectral sensitivity of a photographic material is a very important characteristic as it determines to a large extent the tones in which colored objects are rendered.

The determination of spectral sensitivity involves the isolation of comparatively narrow bands of the spectrum and determining, by one of several methods, the response of the film or plate to radiation within these spectral regions. The most accurate methods of making such measurements require a monochromatic sensitometer [40] which consists essentially of a spectrograph, a means of isolating any desired portion of the spectrum, and a sensitometer.

Sensitometer exposures are made with this instrument in the usual manner, but using monochromatic light instead of white light. From the data accumulated as a result of measurements throughout the spectrum, a spectral sensitivity curve showing the relation between wave length and sensitivity may be plotted. Spectrographic methods of this character, while necessary for a complete analysis of the spectral sensitivity of a film or plate, are lengthy, laborious, and exacting; furthermore, the results obtained by simpler methods are adequate for most purposes.

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[40] Jones, *Photographic Sensitometry.*

One of the most widely used methods of comparing the spectral-sensitivity characteristics of different photographic materials is by means of wedge spectrograms. These are made on a special type of spectrograph whose essential features are shown in Fig. 260. A spectrum of the light source at the extreme right is formed on the sensitive material, placed at the back of the camera to the left, by means of a diffraction grating and the optical system shown. A blackglass wedge placed directly in front of the slit varies the illumination across the spectrum logarithmically, so that the height of the exposed portion of the material at any point indicates the logarithm of the sensitivity at that particular wave length.

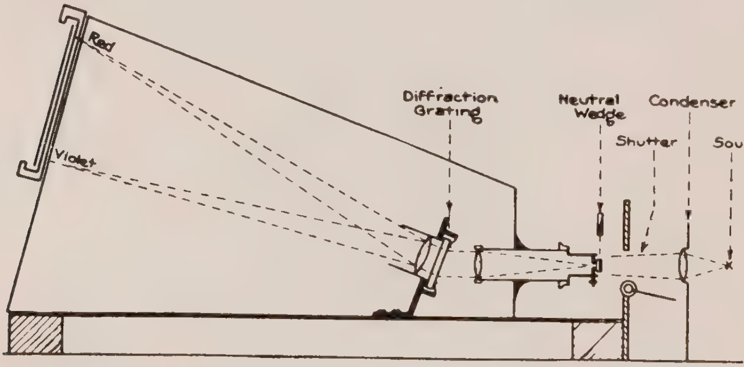


Fig. 260. Cross-Section of Wedge Spectrograph.

Two facts must be kept constantly in mind when using wedge spectrograms as a means of estimating the spectral sensitivity characteristics of a particular film or plate: (1) the curve represents the relation between sensitivity and wave length only in terms of the light source used for the exposure; (2) the absorption of the glass wedge is greater for the short wave region than for the remainder of the spectrum, so that the sensitivity of the film or plate to blue-violet is relatively greater than wedge spectrograms would indicate. This difficulty may be avoided by using rotating sectors in place of an optical wedge; however, it is not serious if wedge spectrograms are used simply for comparing different materials.

A third method consists in determining the response of the material to certain selected regions of the spectrum as isolated by filters. The red, green, and blue tricolor sets are frequently used for this purpose. The relative exposure required with each of the three filters to produce the same result as on a clear strip is determined and expressed as the *filter factor.* The factor thus represents the number of times the exposure for each filter must be multiplied to produce the same effect as a given exposure on the clear strip. This method is identical with that used in determining filter factors.

Color charts, prepared by three-color printing or with pigments, are often recommended as a means of determining spectral sensitivity. The use of these is not advised as the colors obtained in this manner are impure and reflect appreciable amounts of light from all parts of the spectrum so that the results obtained are inconclusive.

EVANS—An Intensity-Scale Monochromatic Sensitometer. J. Opt. Soc. Amer. **30** (1940) 118.

SELWYN AND DAVIES—A Note on the Use of Color Charts in Photography. Phot. J. **78** (1938) 122.

CHAPTER XIV

THE PHOTOGRAPHIC REPRODUCTION OF TONE

A photograph may be made either for the purpose (1) of producing an image which will excite in the mind of the observer the same sensation as that produced by the original or (2) of conveying a certain impression which is desired for its artistic effect. Since photography is essentially a factual method of reproduction, it is probable that in the larger number of cases the first of these is the primary, if not the sole, objective. The extent to which this is possible depends upon the ability of the photographic process to reproduce the brightness of each elementary area in the object. A careful analysis of the various processes involved, as well as an analysis of those factors upon which depends the operation of our visual perception, is obviously essential in the determination of the faithfulness of tone rendition under any given set of conditions.

The visual impression produced by any subject depends upon a number of factors, among which the most important are physical brightness, brightness difference or contrast, and hue. So far as the ordinary processes of photography are concerned, the first two are by far the more important since these may be reproduced with considerable fidelity, while hue can only be suggested. It is, therefore, of preeminent importance that the problem of tone reproduction be thoroughly considered if one hopes to depict the true tonal relationships of an object in a lifelike manner.

Simplifying Assumptions.—In order to bring the theory of photographic tone reproduction within the limits of a single chapter, it will be necessary to make certain simplifying assumptions. First, while most subjects contain one or more colors, in the discussion which follows a monochromatic object will be assumed thus eliminating the complicating factors involved in the reproduction of the color sensation. This simplification becomes necessary, since, in general, the spectral sensitivity of the photographic plate is radically different from that of the human eye. Secondly, we shall further assume that all photographic deposits are non-selective and, therefore, have identical visual and photographic density values.

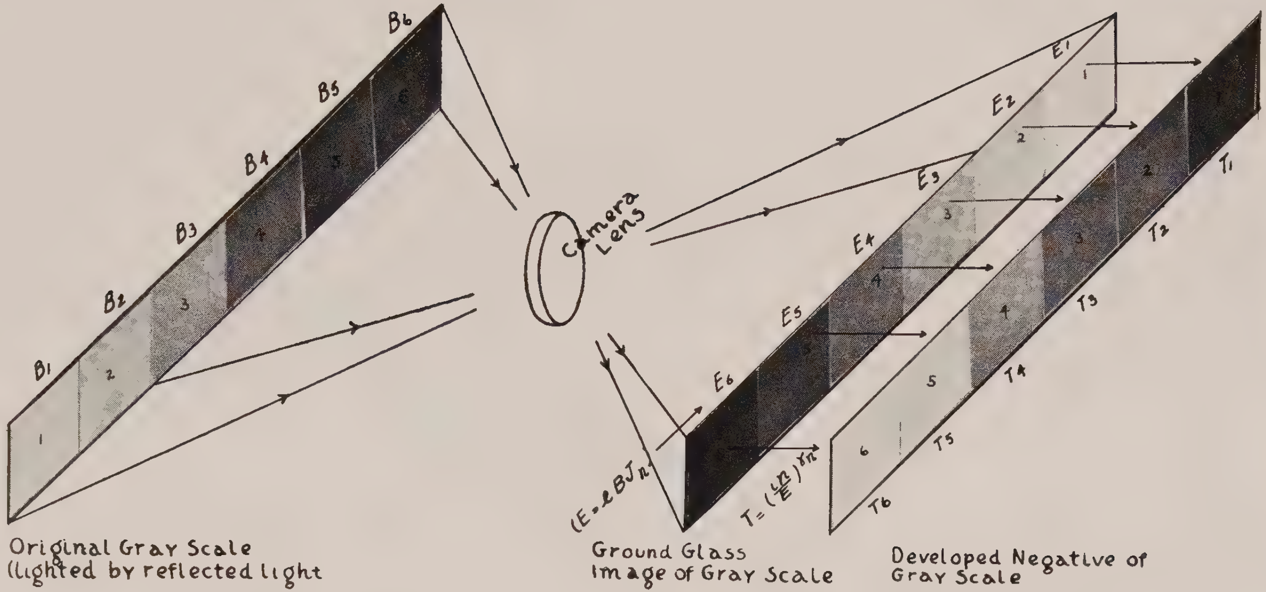


FIG. 261. Schematic Representation of the Rendition of a Scale of Grays in the Negative.

Tone Rendition of a Neutral Grey Object.—For convenience, the object to be reproduced will be regarded as consisting of a scale of neutral brightnesses lighted by reflected light. From the negative a lantern slide is made, which in turn is projected on a white screen. Let B_1, B_2, B_3, . . . represent the measured brightnesses of the 1st, 2nd, 3rd, . . . steps of the grey scale, and b_1, b_2, b_3 . . . represent the brightnesses of the corresponding steps on the screen. True tone reproduction would be achieved when each brightness of the screen image, b, is directly proportional to the brightness, B, of the corresponding part of the subject photographed.

Figure 261 is intended to represent schematically the set-up used in taking this picture. The step on the grey scale marked B_1 is imaged on the negative as T_1, B_2 as T_2, etc. The exposure (in meter-candle-seconds) reaching the film is directly proportional to the product of the brightness of the subject (in meter-candles) and the time of exposure (in seconds). This may be expressed mathematically as:

$$E = lB\tau_n \tag{1}$$

where E = exposure of the negative material in meter-candle-seconds,
B = brightness of the object in meter-candles,
τ_n = duration of the exposure in seconds,
l = a constant depending for its value upon the character of the image forming system. It may be shown from geometrical optics that $l = \pi/4(f/\text{number})$.[2]

From which it follows that the exposure E_1 for the first step of the grey scale would be represented by $E_1 = lB_1\tau_n$, the exposure for the second step by $E_2 = lB_2\tau_n$, and similarly for other steps.

Let us now further assume that the brightness range of the entire grey scale is such that it may be correctly recorded by the negative material, i.e., it can be recorded upon the straight line portion of the H and D curve of the negative material. Hence, the usual sensitometric formulas will apply. Let T_1, T_2, T_3, . . . represent the transparencies of the 1st, 2nd, 3rd, . . . steps of the negative upon development.

The equation on page — may be rewritten as:

$$T = \left(\frac{i_n}{E_n}\right)^{\gamma_n} \tag{2}$$

where T = transparency of the negative in per cent
i_n = inertia of the negative material in meter-candle-seconds
E_n = exposure given to the negative material in meter-candle-seconds
γ_n = degree of contrast to which the negative is developed, i.e., the slope of the H and D curve of the negative material.

From this we see that $T_1 = \left(\frac{i_n}{E_1}\right)^{\gamma_n}$, $T_2 = \left(\frac{i_n}{E_2}\right)^{\gamma_n}$, etc. for the other steps.

Next, a lantern slide positive is made by contact printing form this negative. This operation is represented schematically in Fig. 262.

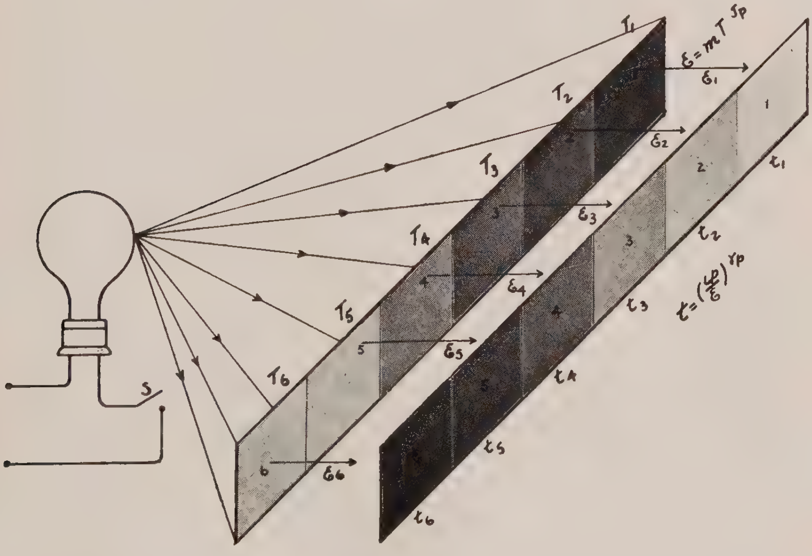


Fig. 262. Reproduction of Negative on Positive Transparency (Lantern Slide).

Here the exposure (in meter-candle-seconds) for any point on the lantern slide is directly proportional to the transparency of the corresponding point of the negative and to the time illuminated. This may be represented mathematically as

$$\mathcal{E} = mT\tau_p \tag{3}$$

where $\mathcal{E}$ = exposure received by the positive material, in meter-candle-seconds,
T = transparency of the negative in per cent,
τ_p = time of illumination in seconds,
m = intensity of illumination on the negative in meter-candles. (This factor is solely a function of the design of the printer.)

The exposure $\mathcal{E}_1$ given the first step of the lantern slide will be represented by $\mathcal{E}_1 = T_1\tau_p$, the second step by $\mathcal{E}_2 = mT_2\tau_p$, etc. Let us now assume that the transparency scale of the negative is such that by selecting the proper printing time, it may be printed within the latitude of the positive material. If t_1, t_2, t_3, $\cdots$ represent the transparencies of the 1st, 2nd, 3rd, $\cdots$ steps of the lantern slide upon development, then

$$t = \left(\frac{i_p}{\mathcal{E}_p}\right)^{\gamma_p} \tag{4}$$

where t = transparency of the positive in per cent,
i_p = inertia of the positive material in meter-candle-seconds,
$\mathcal{E}_p$ = exposure given to positive material in meter-candle-seconds,
γ_p = degree of contrast to which the positive is developed, i.e., the slope of the H and D curve of the positive material.

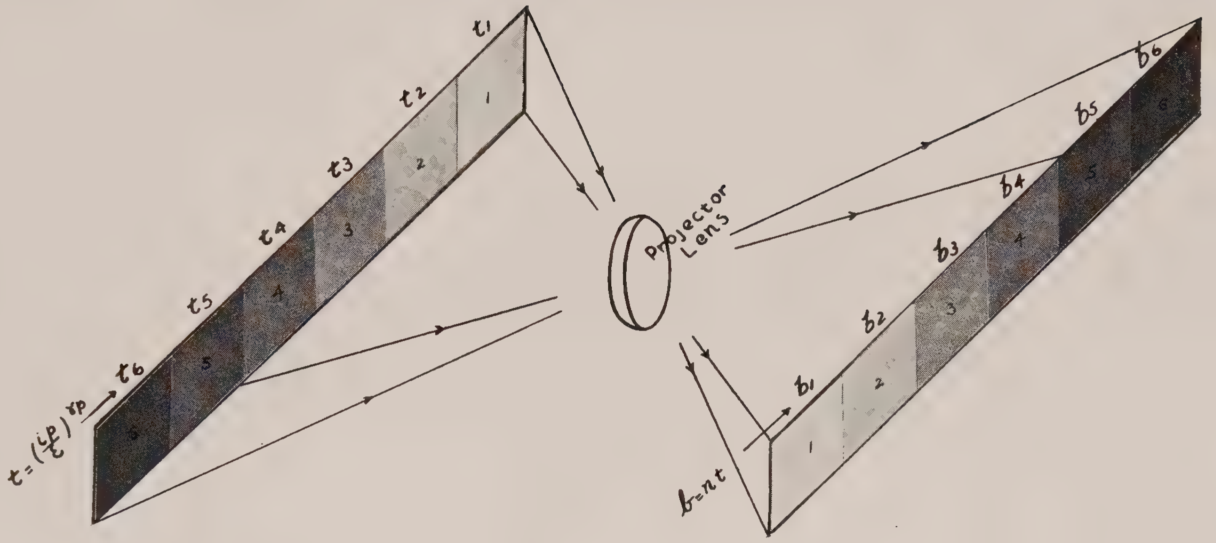
From this it follows that $t_1 = \left(\frac{i_p}{\mathcal{E}_1}\right)^{\gamma_p}$; $t_2 = \left(\frac{i_p}{\mathcal{E}_1}\right)^{\gamma_p}$, etc., for the other steps.

Now if this slide is placed in a suitable projector and the projected image of the grey scale examined as it appears on the screen (see Fig. 263), the brightness of any step of the grey scale will be directly proportional to the transparency of the corresponding step on the slide, or,

$$b = nt \tag{5}$$

where b = screen brightness of any particular section of the screen, in meter-candles,
t = transparency of the corresponding section of the lantern slide positive in per cent,
n = a factor representing the amount of light incident upon the slide in the projector ($1/(f/\text{number})^2$).

Therefore, the screen brightness of the first step of the grey scale will be represented by $b_1 = nt_1$, the second step by $b_2 = nt_2$, etc.



Lantern Slide Positive of Gray Scale

Screen Image of Gray Scale

FIG. 263. Schematic Representation of the Formation of a Screen Image of the Scale of Grays in the Positive Transparency.

We are now in a position to analyze the conditions which must be satisfied if the screen brightness, b, at any point is to be directly proportional to the brightness, B, of the corresponding point in the subject. Starting with Eq. 5 and substituting the value of t as given by Eq. 4, we have

$$b = n\left(\frac{i_p}{\mathcal{E}}\right)^{\gamma_p}.$$

Substituting the value for $\mathcal{E}$ as given by Eq. 3, we have

$$b = n\left(\frac{i_p}{mT\tau_p}\right)^{\gamma_p}.$$

Substituting the value for T as given by Eq. 2, we have

$$b = n\left[\frac{i_p}{m\tau_p\left(\frac{i_n}{E_n}\right)^{\gamma_n}}\right]^{\gamma_p}.$$

And finally substituting the value for E as given by Eq. 1 we have

$$b = n\left[\frac{i_p}{m\tau_p\left(\frac{i_n}{lB\tau_n}\right)^{\gamma_n}}\right]^{\gamma_p}. \tag{6}$$

If, for the sake of simplicity, we make the limiting assumption that both the negative and positive are developed to a gamma of unity, i.e.

$$\gamma_n = \gamma_p = 1,$$

then Eq. 6 reduces to the form

$$b = \frac{nl}{m} \cdot \frac{\tau_n}{\tau_p} \cdot \frac{i_p}{i_n} \cdot B, \tag{7}$$

which immediately indicates that b is directly proportional to B when both γ_n and γ_p are unity. It may be shown algebraically that the γ values of the negative and positive need not be unity individually, but only their product be unity. For example, if the negative is developed to a gamma of 0.5 and the positive to a gamma of 2.0, the reproduction of tone values is the same as would be secured were both the gamma of the negative and positive equal to unity. Thus it may be concluded that for the proportional reproduction of the brightness differences of the original, the product of the negative and positive gammas should be unity. In other words,

$$\gamma_n \cdot \gamma_p = 1.$$

However, it is important to remember that this entire argument has been built upon the following limiting assumptions:

1. That all the areas of the object photographed are both visually and photographically colorless.
2. That all the densities involved lie on the straight-line sections of the H and D curves.

Effect of Gamma Product on Tone Reproduction.—It will be of interest to consider how far the γ product of the negative and positive may deviate from unity without seriously affecting the reproduction or rendition of tone values. Assume, for example, a landscape in which the brightness range is approximately 32 to 1—that is, the brightness of the highest light is 32 times that of the deepest shadow. Denoting the highlight brightness by B_1 and the shadow brightness by B_2, the brightness range of the scene is:

$$\frac{B_1}{B_2} = 32.$$

Since most negative materials possess a latitude of 128 to 1 or more, it is possible with the proper camera exposure to record this range of brightnesses on the straight-line portion of the D log E curve. Then the relation between the transparency of any given area of the developed negative and the brightness of the corresponding part of the subject may be represented as

$$T = \left(\frac{i_n}{E_n}\right)^{\gamma_n}.$$

By substitution it can be shown that the transparency range T_2/T_1 of the negative will be given by

$$\frac{T_2}{T_1} = \left(\frac{B_1}{B_2}\right)^{\gamma_n}. \tag{8}$$

With the aid of Eq. 4, it may be shown also that the transparency range of the positive is given by

$$\frac{t_1}{t_2} = \left(\frac{B_1}{B_2}\right)^{\gamma_n\gamma_p}. \tag{9}$$

An examination of Eq. 9 reveals that the gamma-product of the negative and positive is an exponential quantity. This means that even a slight deviation of the gamma product from unity will produce a relatively large change in the faithfulness of the tone rendition. When the gamma-product is larger than unity, the reproduction exhibits a greater contrast than the brightness range of the subject photographed; and when less than unity, the reproduction has less contrast than the original.

Enhancement of Contrast by Increasing Gamma Product.—For certain scientific applications it may be desirable to enhance the contrast of the original subject by developing both the negative and positive to a gamma-product greater than unity. In photomicrography, for example, details on the microscope slide which are invisible to the eye may frequently be effectively increased in this manner. This is possible since the eye has a minimum contrast sensitivity of approximately two per cent. Hence, brightness differences on the microscope slide which are less than two per cent will be indistinguishable to the eye. By extending the time of development it is quite possible to attain a gamma value of 2.0, while a gamma of 3.0 can be secured with some negative materials. Assuming a gamma of 3.0 for both the negative and positive, the gamma-product becomes 9.0. By such treatment, a brightness difference as small as 0.30% can be increased to $0.30 \times 9 = 2.7\%$ in the positive and therefore will become readily distinguishable to the eye.

The converse of this situation frequently arises. It may be necessary, for example, to photograph a subject where the brightness range is greater than that which can be recorded on the positive material available. In this case, it is necessary to develop both the negative and positive so that the product will be less than unity in order to secure faithful tone rendition.

A Graphical Solution of Tone Reproduction.—Thus far, only the correct reproduction on the screen of the actual physical brightnesses present in the object and of the actual contrast relations existing between various areas of the object has been considered. However, when the subjective impression produced by a given brightness is entirely dependent upon the state of adaptation of the observer's eye, it is obvious that such treatment as given above cannot represent a complete solution. The problem may be divided into two distinct phases: (1) the objective phase, which deals solely with the reproduction of the actual physical brightnesses and is capable of mathematical analysis; and (2) the subjective phase, which includes a consideration of those factors determining the nature of the subjective impressions produced by the action of a given physical stimulus under various conditions, and requiring the use of psycho-physical methods and data for its adequate treatment.

Heretofore, it has been assumed that all of the densities involved lie on the straight-line sections of the negative and positive H and D curves. In practice, this is not usually the case; it frequently becomes necessary to use the toe of the negative curve and both the toe and shoulder of the positive curve. An analysis of the rendition of tone values under these conditions becomes too complicated to express conveniently in mathematical language. However, a graphical solution, by Jones of the Eastman Kodak Research Laboratory, offers a most ingenious method of making this analysis. Fig. 264 presents this solution, the necessary curves being plotted in four quadrants designated for reference as I, II, III, and IV.

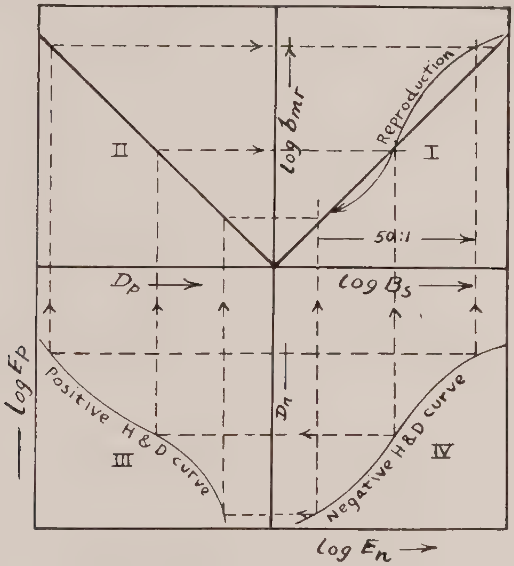


FIG. 264. Graphical Method of Determining the Faithfulness of the Tone Reproduction with Hypothetical, (*a*) Negative and (*b*) Positive Materials.

The fourth quadrant contains the characteristic H and D curve of the negative material;

The third quadrant, the characteristic H and D curve of the positive material, and

The second quadrant shows the variation in the response of the eye when viewing the original subject and when viewing the reproduction (the illuminated positive).

The first quadrant shows the extent to which accurate tone rendition has been achieved. The curve therein compares the visual sensation produced by the reproduction with that of the original. If the tone values are faithfully rendered, this curve will of necessity be a straight line at an angle of 45° to the axis.

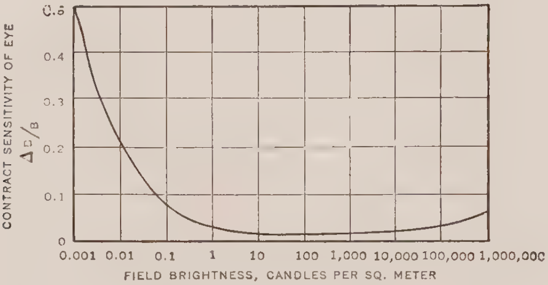


FIG. 265. Curve Representing the Relative Contrast Sensitivity of a Normal Human Eye at Different Levels of Field Brightness Taken from Data of König and Brodhun and Adjusted for the Size of the Natural Pupil According to Data Supplied by Reeves.

In most of the cases encountered in practice, both the subject and the reproduction are viewed under adaptation levels which lie on the straight-line portion of the visual sensation curve (Fig. 265). Therefore, the relative subjective contrast function shown in the second quadrant of Fig. 264 appears as a straight line through the origin at 45°.

From a study of the reproduction curve in the first quadrant of Fig. 264, it will be observed that the tone reproduction curve deviates quite markedly from linearity. The magnitude of the departure from an exact reproduction of the subject *brightness* is given by the length of a perpendicular line limited by the straight-line curve and the reproduction curve and drawn through the point considered; while the relation of the slopes of the curves at corresponding points determines the magnitude of the departure from exact reproduction of the *contrast* in the object at the point considered.

Analysis of Reproduction Curves.—The reproduction curve in Fig. 264 also indicates that the maximum contrast is secured from densities lying on the straight-line sections of the H and D curves of both the negative and positive materials. It will also be noted that in the hypothetical example chosen, the shapes of the toe and shoulder of the negative and positive curves work against one another in such a manner as to lower the reproduced contrast from these regions. Loss of subject detail in both the shadows and highlights is the result of this reduced contrast. In practice this difficulty is avoided by using negative and positive materials which do not have these obvious faults in curve shape. Figs. 266, 267, and 268 are presented to show how the faithfulness of reproduction is affected through the utilization of negative and positive materials possessing various characteristics.

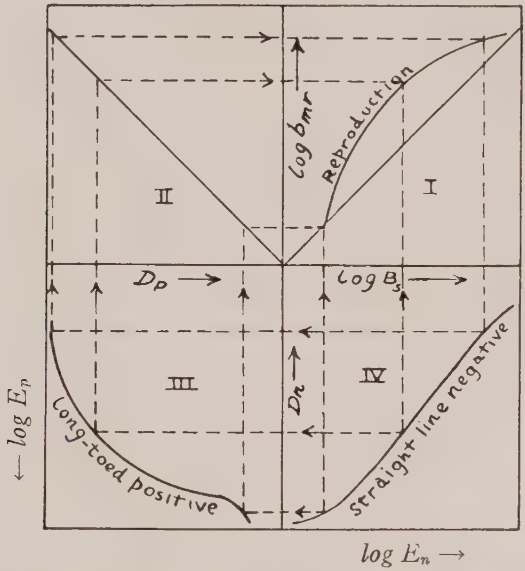


Fig. 266. Graphical Representation of the Accuracy of Tone Reproduction Obtained when Printing a Straight-Line Negative on a Positive Material with a Long Toe.

From Fig. 266 it will be observed that the contrast in the shadows is enhanced, while that in the highlights is reduced. This occurs when the negative densities lie on the straight-line portion of the *D* log *E* curve and are printed on a positive material having a long toe. From Fig. 267 it is seen that shadow contrast is lowered and highlight contrast enhanced when a negative in which many of the densities lie in the toe portion of the curve is printed on the straight-line portion of the positive material. Fig. 268 presents a case where the straight-line portions of both the negative and positive materials are used exclusively. Here the reproduction curve in the first quadrant is a straight line, which indicates that the tone rendition is correct.

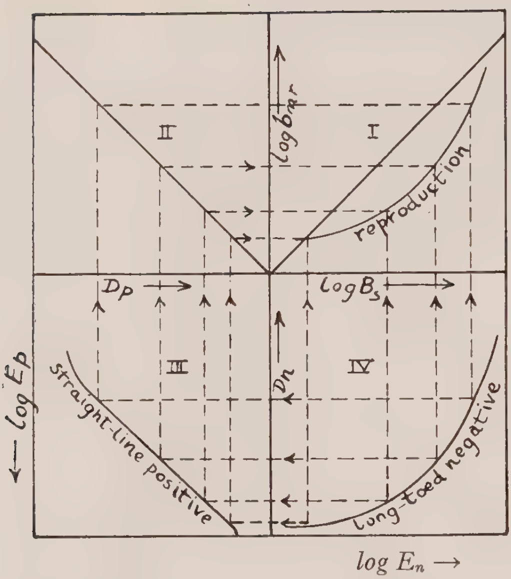


FIG. 267. Graphical Representation of the Accuracy of Tone Reproduction Obtained when Printing a Negative Utilizing the Toe Portion of the *D* log *E* Curve on the Straight-Line Portion of the Positive Material.

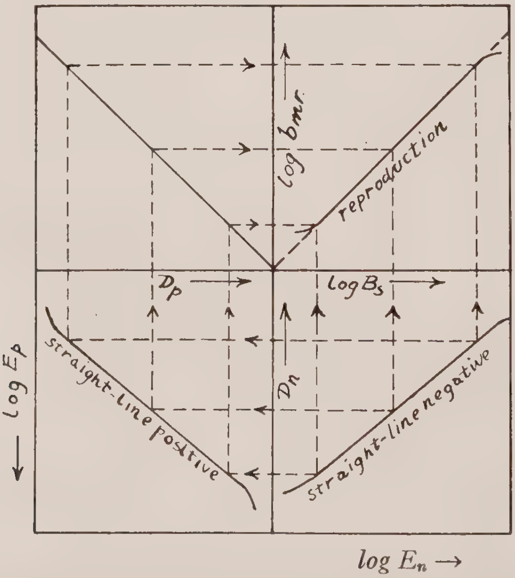


FIG. 268. Graphical Representation of the Accuracy of Tone Reproduction Obtained when Printing a Negative Utilizing the Straight-Line Portion of the *D* log *E* Curve on the Linear Portion of the Curve of the Positive Material.

However, a positive material having as short a toe and as long a straight line as that shown in Fig. 268 is not readily obtainable in practice. Moreover, it is not at all necessary to use straight line negative and positive materials in order to obtain a correct, straight line reproduction. Any curvature which occurs in the negative can be compensated by a corresponding curvature in the positive. Printing a negative having a bow shaped curve on a positive material which also has a bow shaped curve can result in a high quality print, the reproduction curve of which will either be a straight line or a curve which is so nearly a straight line that the quality is entirely satisfactory. A typical example is presented in Fig. 269. Quadrant IV contains a normal negative curve and quad-

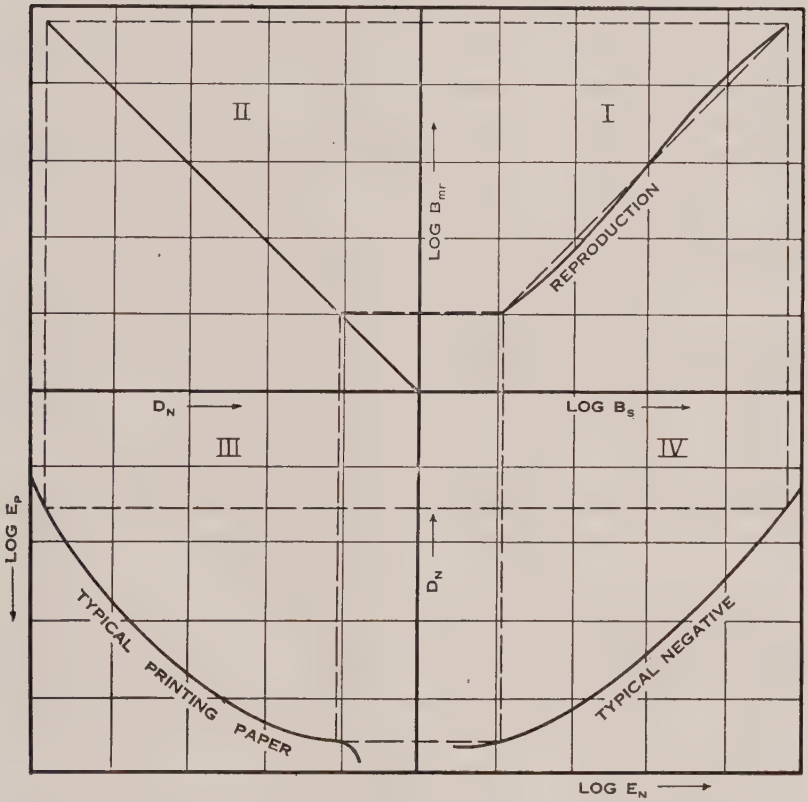


FIG. 269. Tone-Reproduction Diagram Showing How it is Possible to Obtain Linear Reproduction by the Matching of Curved Portions of the *D* log *E* Curves of the Negative and Positive Materials.

rant III contains a curve for a typical positive printing paper. A study of this diagram will show that the reproduction curve turns out to be a straight line, or very nearly so, because the flat part of the negative is printed on the steep part of the positive while the steep part of the negative is printed on the flat part of the positive. As Jones[1] has emphasized, for correct, objective tone reproduction, the positive and negative curves should be mirror images of each other.

The above analysis shows that there is sound theoretical justification for the very common photographic practice of making negatives which use a considerable portion of the toe of the negative material, and it shows that there is good reason for the common use of long toed positive materials. The old Hurter and Driffield theory, which assumed that straight line negatives and straight line positives were required for correct, straight line reproduction, is being abandoned by most of the leading research workers in the field of photographic tone reproduction.

Tone Reproduction on Printing Papers.—The characteristic curve of printing papers is similar to that of negative materials except that the straight-line portion is shorter. A good negative material is capable of recording proportionally a brightness range of 1 : 128 or more. Since printing papers depend upon reflected rather than transmitted light, they are limited to the difference between the amount of light reflected from the white paper and that reflected from the deepest black which the paper will produce. The maximum black obtainable with any paper varies with the emulsion and the surface of the paper. With a matt paper, the difference in the amount of light reflected from the unexposed paper and the maximum black may be in the ratio of 1 : 15; with glossy papers, the ratio is greater, usually from 1 : 50 to as high as 1 : 100. Hence, it is possible to reproduce the full scale of brightness in many subjects photographed only if the entire scale of the paper is used.

For subjects having brightness scales exceeding the scale of the paper, it is necessary to sacrifice the reproduction of those parts of the tone scale that are of minor importance in order that the portion holding the greater subject interest may be properly rendered.

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[1] Jones, *J. Franklin Inst.* **227** (1939) 317.

Jones and Morrison—The Sensitometry of Photographic Papers. J. Franklin Inst. **228** (1939) 755.

Renwick—Difficulties in Translating the Theory of Tone Reproduction into Practice and the Sensation of Contrast (Tenth Hurter and Driffield Memorial Lecture). Phot. J. **77** (1937) 6.

In practice, the tone reproduction obtained on a printing paper is controlled (1) through the choice of a paper the exposure scale of which is suitable for the opacity range of those portions of the negative which represent the most interesting parts of the subject and (2) by adjusting the printing exposure to obtain the tonal differences which are regarded as suitable for the subject as a whole.

Three examples may serve to show how these principles are applied to the problem of tone reproduction in printing.[2]

I. Suppose one wishes to print a rather contrasty negative of an open landscape having a dense sky without clouds in which the interest lies chiefly in the foreground. If a paper is chosen having a scale which will record the deepest shadows in both the foreground and sky, the foreground detail will fall on the overexposure portion of the paper curve and hence will be flat and lacking in contrast. For such a case it would be better to regard the scale of the negative as the difference between the lowest and the highest density in the foreground alone. Then, if a paper is selected having sufficient latitude to record this range, satisfactory rendering will be obtained for the most important part of the subject.

II. In a similar landscape where the chief interest is in the cloud formations, the conditions would be exactly the reverse of Case I. Here it would be the highlight gradations that we would attempt to record faithfully.

III. Let us now consider a scene in which the objects of major interest consist of middle scale values surrounded by strong highlights and shadows. Under these conditions the negative gradation is very much greater than can be recorded on paper. Consequently we shall endeavor to render properly the half-tone region and let the shadows and highlights take care of themselves. This can be achieved by selecting the proper paper and giving the correct exposure to record the object of greatest interest on the portion of the H and D curve, having good gradation. Obviously the rendition of the highlights and shadows will be distorted, the amount of distortion depending upon the shape of the toe and shoulder of the characteristic curve of positive material. Naturally, the greater the latitude of the paper, the more perfectly the extremes will be reproduced.

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[2] Mees, Jones and Nutting, *Phot. J.* **54** (1914) 342; Mees, **64** (1924) 311.

CHAPTER XV

THE REPRODUCTION OF COLOR IN MONOCHROME

Tone reproduction, in the case of an object free of color, involves only the reproduction of the brightness differences, or contrast, between different parts of the object. A white block against a dark background (Fig. 270), for example, when lighted from one side contains areas which, apart from their shape, differ only in brightness, i.e., in the amount of white light reflected. Many, if not most subjects, however, contain areas which differ in *color*. The visual contrast between different parts of the subject in this case is not necessarily the result of differences in the amount of light reflected as in the kind, or color, of light reflected. Visually, colors differ in respect to hue, saturation and brilliance or lightness. *Hue* is the characteristic of color which distinguishes it from white or grey; i.e., green, blue, red, etc. *Saturation* has reference to the distinctness or vividness of hue, while brilliance, or lightness, is the intensity of the visual response to a color as compared with a tone of gray; i.e., the characteristic which enables a color to be classified as the equivalent in lightness to some member of a series of grays ranging from black to white. The contrast between two colors may be the result, therefore, of a difference in hue, in saturation, in brilliance or in any combination of these. Differences in hue and saturation cannot be reproduced, other than in color photography, except as differences in brightness, as we are limited to the differences in brightness produced by the deposits of silver, or pigment, forming the image. It is necessary, therefore, to reproduce differences in subject contrast which may be due to a difference in either hue, saturation, brilliance or all three, by means of the last mentioned characteristic alone.

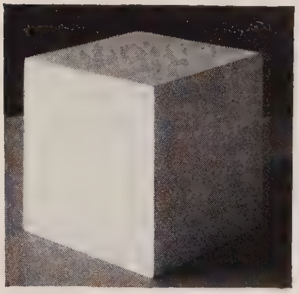
FIG. 270.

It is necessary to examine first, therefore, the relation between the wave length of radiation and the resulting sensation; i.e., the visual function, or the color-brilliance (lightness) characteristic.

Spectral Response of the Eye and Typical Photographic Materials.—The relation between the wave length and visual response for a light source having a color temperature of 5400° K. (the accepted standard for noon sunlight) is represented by curve *A* in Fig. 271 from which it is evident that the maximum response of the eye occurs at a wave length of approximately 550 mμ, or in the yellow from which points it drops sharply to the limits at wave lengths of approximately 400 mμ in the violet and 700 mμ in the deep red. The wave length response of typical blue-sensitive, orthrochromatic and panchromatic materials under the same conditions is shown by curves *B*, *C* and *D* respectively.[1] It will be observed that all three show a maximum response in the blue-violet between 400 mμ and 500 mμ. Ordinary, or blue-sensitive materials are for all practical purposes insensitive at wave lengths greater than 525 mμ; therefore, those colors which appear most brilliant to the eye are reproduced almost black. The sensitivity of

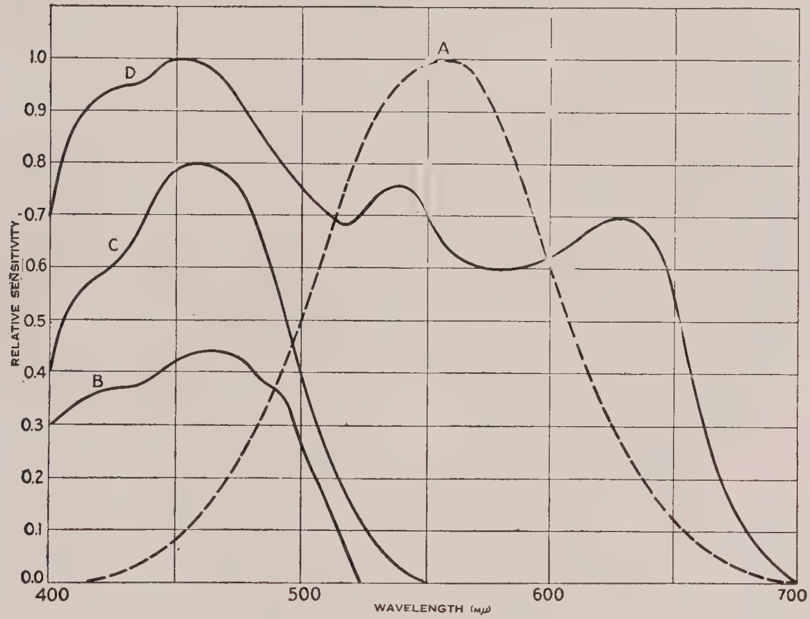

FIG. 271. Curves Representing the Relation Between the Wave-Length and the Response of (*A*) the Eye, (*B*) Blue-sensitive, (*C*) Orthochromatic, and (*D*) Panchromatic Materials for Noon Sunlight (5400° K).

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[1] See also the wedge spectrograms on pages 488, 489.

orthochromatic materials extends to a wave length of from 550 mμ to nearly 600 mμ depending upon the sensitizer employed, so that materials of this type are sensitive to green and yellow as well as to violet and blue. The range of sensitivity of panchromatic materials is approximately the same as that of the eye but the distribution of sensitivity is quite different. Thus, while the use of panchromatic materials results in an improvement in the rendering of color as compared with blue-sensitive or orthochromatic materials, the reproduction with a panchromatic material with sunlight does not correspond with the color brilliance response.

Effect of the Light Source.—In Fig. 272 are shown spectral energy curves representing (A) average noon sunlight (5400° K.); (B) incandescent tungsten illumination (3400° K.) and (C) incandescent tungsten illumination (2360° K.).[2] It is evident from a comparison of these curves that the spectral energy distribution of both of the tungsten sources is quite different from that of noon sunlight, the energy output of tungsten radiation being lower than that of sunlight for the shorter wave lengths and relatively greater for the longer wave lengths. Since the *effective* distribution of spectral sensitivity depends upon the spectral energy characteristics of the light source, as well as the spectral sensitivity response of the photosensitive material, it is clear that the use of either of the tungsten sources represented will result in sensitivity curves which are lower in the short wave region and higher in the long wave region than those in Fig. 271.

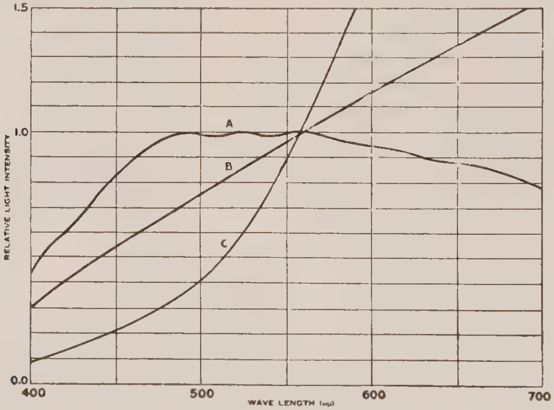

FIG. 272. Spectral Energy Curves, (*a*) Average Noon Sunlight (5400° K), (*b*) Incandescent Tungsten Illumination (3400° K), and (*c*) (2360° K).

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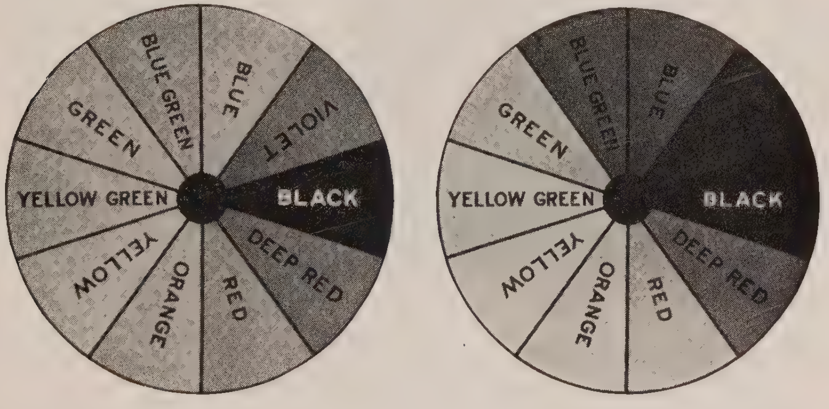
[2] For other spectral energy curves see Chapter V.

A natural consequence of the alteration in the spectral response of a photographic material brought about by a change in the spectral distribution of energy in the light source used for the exposure, is a difference in the relative brightnesses in which different colors are reproduced by the photographic material. In Fig. 273 is shown a reproduction of a color chart photographed on a panchromatic material, at the left by sunlight and at the right by tungsten illumination.



(Left) (Right)

FIG. 273. Reproduction of a Color Chart Photographed on a Panchromatic Material, (left) in Sunlight and (right) in Incandescent Tungsten Illumination.

A comparison of the relative brightnesses in which the different colors of the original are reproduced by the two light sources, shows that the employment of tungsten illumination, with its greater abundance of long wave radiation, has resulted in yellow, orange and red being reproduced relatively lighter and violet and blue darker than with sunlight. The relative brightnesses in which different colors are reproduced depend on the distribution of spectral sensitivity with the particular light source used for the exposure. The greater the effective sensitivity in any particular part of the spectrum, the greater the density of the negative and the lighter the tone of gray in which the corresponding color sensation is represented in the print.

Light Filters.—In practice, the rendering of color by a photographic material is controlled so as to produce the result desired by using a *light filter*.[3] A light filter may be defined as an optically homogeneous (i.e., non-turbid or scattering) medium possessing selective or differential absorption; i.e., the absorption, or density, varies with the wave length. The curve in Fig. 274, for example, represents

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[3] Also termed color filter, color screen, ray filter.

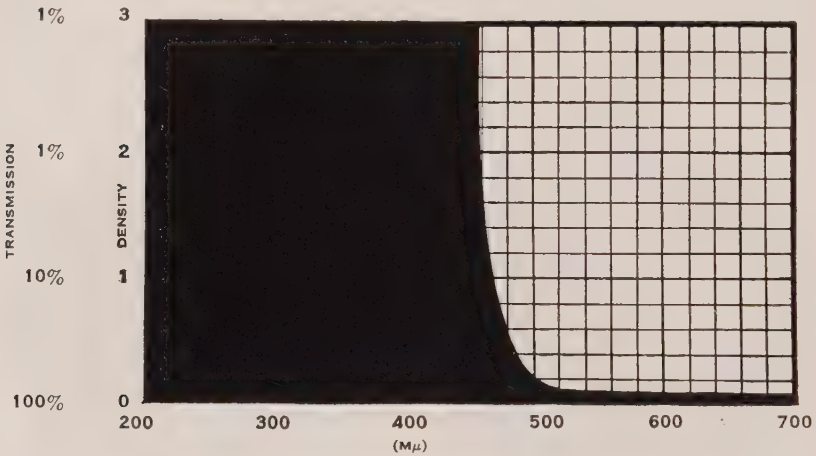

Fig. 274. Spectrophotometric Curve of the Transmission, (Light) Absorption, (Dark) Characteristics of a Yellow Filter.

the relation between absorption and wave length for a typical yellow filter. The dark portions represent the absorption, or density, in relation to wave length, while the clear portion represents the transmission at each wave length. Spectrophotometric curves of this kind are determined by means of a spectrophotometer. In this instrument, a spectrum is formed by means of a prism or a diffraction grating and radiation of any desired wave length is isolated by a narrow slit. One half of the radiation thus isolated is then caused to pass through the filter which is being examined and the intensity of the radiation transmitted by the filter is measured by comparing it, in a suitable photometer, with the other half of the beam of light which has not been subjected to the absorbing action of the filter. In this way, values for the transmission of the filter at different wave lengths are obtained. These values are then plotted as a function of wave length to form a curve which shows the spectral absorption characteristics of the filter.[4]

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[4] The absorption of filters is frequently represented by wedge spectrograms. These are usually made in an instrument of the type shown in Fig. 260, the filter being placed between the light source and the slit of the spectrograph. While useful for comparative purposes, wedge spectrograms necessarily represent filter characteristics in terms of some particular light source, and photographic material.

The effect of a filter on the distribution of sensitivity for a particular photographic material may be found by multiplying wave length by wave length, the ordinates of the curve representing the spectral response of the film or plate by those of the curve representing the transmission characteristics of the filter. Both curves, however, must be for light of the same color temperature. In Fig. 275, for example, curve *A* represents the spectral sensitivity of a panchromatic material to light of tungsten quality, *B* is the transmission curve of a yellow filter plotted on the same basis. By multiplying the ordinates of curve *A* by those of curve *B* at corresponding wave lengths, curve *C* representing the distribution of sensitivity of the film with the filter is obtained.

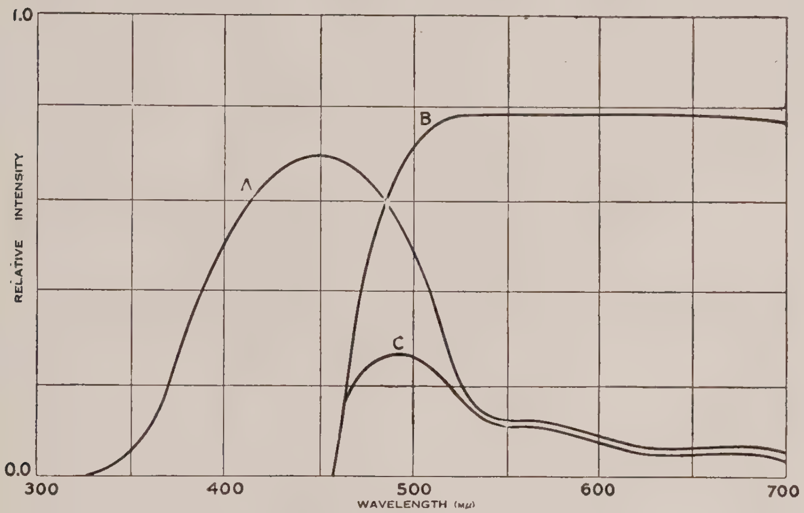

Fig. 275. Curves Representing (*A*) The Spectral Sensitivity of a Particular Panchromatic Material, (*B*) the Transmission Curve of a Yellow Filter, and (*C*) the Distribution of Sensitivity with the Filter.

Since the relative brightnesses in which colors are reproduced by a photographic material depend upon its effective distribution of sensitivity, it is evident that the change in spectral sensitivity characteristics brought about by the use of a filter is accompanied by a similar change in the reproduction of color. The filter in Fig. 274, for example, absorbs violet and blue and transmits green, orange and red. Thus the exposure for violet and blue is reduced so that these colors are rendered darker while green, orange and red are rendered lighter in comparison.

In other words, a filter causes colors of those wave lengths which it absorbs to be rendered darker while those in its transmitting band are rendered *relatively* lighter.

Filter Factors.—Since the employment of a filter results in the absorption of light in a spectral region to which the photographic material is sensitive, it is obvious that the effective illumination is reduced, necessitating an increased exposure. The number of times the exposure must be increased when using a filter is known as the *filter factor.*

The filter factor depends on (1) the absorption spectrum of the filter, (2) the spectral sensitivity of the photographic material with which it is used and (3) the distribution of spectral energy in the illumination incident on the subject photographed.

Thus a filter which absorbed totally all radiation between 300 $m\mu$ and 400 $m\mu$ (violet and blue) would reduce the sensitiveness of an ordinary (blue-sensitive) material almost to the vanishing point. In the case of an orthochromatic material, the effect on sensitiveness would be less because a larger proportion of the total sensitivity lies in spectral regions which are not absorbed by the filter. The effect on a panchromatic material will be even less and for the same reason. Hence, the filter factor for the same filter will be much greater for ordinary than for orthochromatic material and still less for panchromatic material. With a filter transmitting between 300 $m\mu$ and 400 $m\mu$ and absorbing the remainder of the spectrum, the effect will be reversed.

The filter factor varies also with the distribution of energy in the illumination incident on the subject. The greater the proportion of the total energy which lies in the spectral region transmitted by the filter, the lower the filter factor.

For example, tungsten radiation contains a larger proportion of yellow, orange, and red light and less violet and blue than daylight. Therefore, the factors for yellow, orange and red filters are lower for tungsten than for daylight. The reverse is true, however, of a blue filter.

The factor of a filter, therefore, cannot be expressed except in terms of a particular sensitive material and source of illumination.

Determination of Filter Factors.—The filter factor may be calculated by integration from curves representing the distribution of spectral sensitivity with and without the filter. In Fig. 275, for example, curve A represents the spectral sensitivity of a particular panchromatic film without a filter; B is the transmission curve of the filter, and C the wave length-response curve of the film with the filter. The total photographic effect produced without a filter is proportional to the area under curve *A*, and with the addition of a filter, the area under curve *C*. By measuring these areas with a planimeter and dividing the area under curve *A* by that under curve *C* the filter factor under these conditions is obtained.

In practice, however, filter factors are usually determined by sensitometric methods because of their greater convenience.

If two sensitometric strips are exposed, one with and one without the filter, the *D* log *E* curves plotted and the speed in each case determined by any of the usual methods, the ratio of the speed with the filter to that of the film without a filter will be the filter factor. In Fig. 276, for example, curve *A* is the *D* log *E* curve for a particular film without a filter, while curve *B* represents the same film exposed under the same conditions, but with a filter, both strips being developed for the same

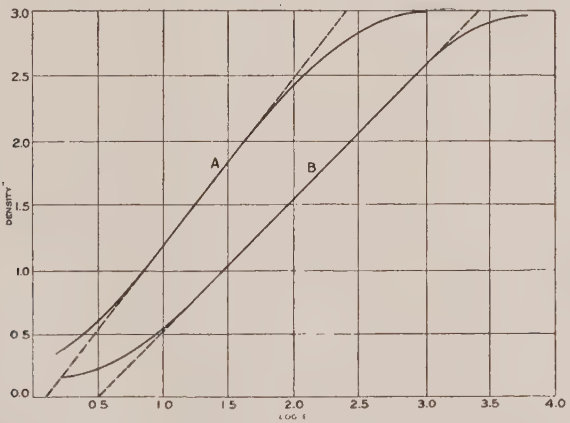

FIG. 276. *D* log *E* Curves Developed for the Same Time Exposed, (*A*) Light of Sunlight Quality, no Filter, (*B*) with a Filter.

DAVIS—A New Method of Measuring the Factors of Light Filters. Phot. J. **61** (1921) 169.

JONES AND MCFARLANE—The Precise Measurement of Filter Factors and Photographic Reflecting Powers. J. Soc. Mot. Pict. Eng. **19** (1932) 361.

LANGER—Determination of Filter Factors According to Wedge Difference Method. Phot. Ind. **32** (1934) 818.

SHARANOV—Calculation of Filter Factors. Kino. Phot. Chem. Ind. No. 3 (1938) 15.

TUPPER—Filter Factors. Photo.Tech. **1** (1940) 29.

time and plotted on the same log E scale, the exposure values being those produced in the sensitometer *without* a filter. It will be noted that although both strips were developed together for the same time, the gamma of curve A is greater than that of B. In other words, one of the results of using a filter has been to increase the gamma obtained with a given time of development. This indicates that gamma depends upon the spectral characteristics of the light used for the exposure as well as on the conditions of development. Since the two D log E curves are not parallel, it is clear that if the filter factor is calculated from the ratio of the two speed values as determined from the inertia, negatives exposed in accordance with the factor as thus determined will match in density only at some point in the shadow region. The densities of the highlights and halftones of the filter negative will be less than those of the negative made without a filter because of the difference in gamma. Likewise a filter factor determined from the ratio of the exposure required to produce a particular density will result in negatives which match at that density but not elsewhere. The lack of agreement, however, is usually of small importance in general photography if a density is used for calculation which is approximately midway within the usual negative density range. In determining filter factors for three-color photography, the sensitometric strips exposed with and without a filter should be developed to the same gamma and the filter factor determined from the ratio of the exposures for a given density on the straight line portion of the D log E curve.

Practical filter factors may be conveniently determined by photographing a black and white photograph with and without the filter. The photograph should be a neutral black; blue-black or brownish black prints are not advisable. A series of exposures is made, preferably by varying the lens aperture so as to avoid variations in shutter speeds, first without and then with the filter. After development, the series of negatives made with the filter is compared with the other and the images selected which match in the highlight region. The filter factor is calculated from the ratio of the exposures for the two negatives.

Orthochromatic Reproduction.—The correct reproduction of color in terms of its brilliance, or lightness, characteristic is termed *orthochromatic reproduction.* Orthochromatic, from the Greek roots, *ortho* correct and *chroma* color, is used here in its true significance; orthochromatic films and plates, on the other hand, do not produce orthochromatic reproduction but only an improved rendering of color as compared with ordinary or blue-sensitive materials.

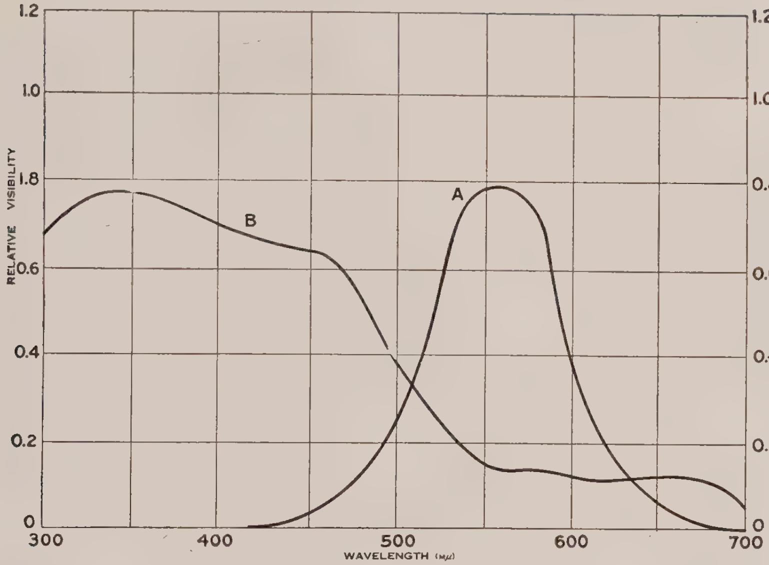

Fig. 277*a*. (*A*) Color Brilliance Curve, and (*B*) the Spectral Sensitivity Curve of a Panchromatic Material.

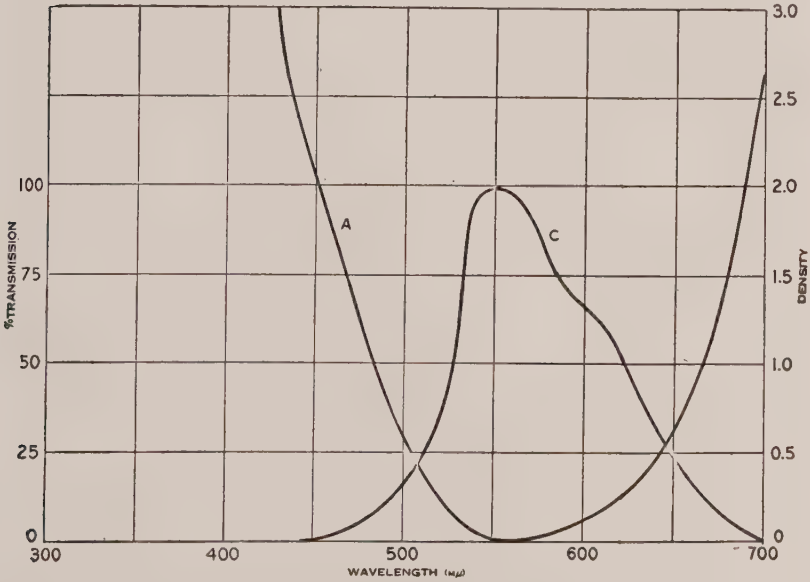

Fig. 277*b*. (*C*) Curve Representing the Transmission of the Filter Required to Produce Orthochromatic Reproduction on the Sensitive Material in Fig. 277*a*.

For orthochromatic reproduction, the effective distribution of photographic sensitivity should correspond with the visual function, i.e., the color brilliance curve. With the sensitive materials and light sources now available, filters are necessary if orthochromatic reproduction is to be obtained. The transmission curve of the filter necessary for orthochromatic reproduction when a particular film or plate is used may be found by dividing the ordinates of the color brilliance curve by those of the curve representing the distribution of sensitivity with wave length for that particular material.

In Fig. 277, for example, A is the color brilliance curve and B the spectral sensitivity curve for a particular panchromatic material to sunlight. In Fig. 277B, C is the curve obtained by dividing the ordinates of curve A at each wave length by those of curve B and represents the transmissions of the filter required to produce orthochromatic reproduction under these conditions. The transmission values may be converted to density by the usual formula $D = \log i/T$ to obtain the density characteristics of the required filter (curve A).

While sensitive materials have been greatly improved in recent years, filters which produce *perfect* orthochromatic reproduction absorb too much light and necessitate too great an increase in exposure to be generally useful. Most orthochromatic filters, therefore, do not produce true orthochromatic reproduction but only what is regarded as a satisfactory approach to it.

From a theoretical standpoint, an orthochromatic filter produces orthochromatic rendering regardless of the spectral energy characteristics of the light source used for the exposure. In other words, a filter which results in orthochromatic reproduction on a given film or plate using sunlight, will correctly reproduce colors *as they appear by tungsten illumination* when used with an incandescent tungsten light source. It is customary, however, to reproduce colors in accordance with their brilliance characteristic in sunlight and, therefore, in practice, lighter filters are used with incandescent tungsten illumination than in sunlight.

In all cases, the filters recommended for orthochromatic reproduction by the manufacturer of the film or plate should be used.

Using Filters for Color Selection.—In practice, orthochromatic reproduction is not always the end in view. Objects are distinguished from their surroundings by *contrast* which may be the result of a difference in brightness or a difference in color. Frequently, parts of the subject may differ but little in brightness and yet the contrast to the eye may be considerable because of a difference in color. The contrast between a bright red apple amidst a cluster of green leaves, for example, is very striking to the eye. Actually, however, the brightness difference is small and when photographed on a panchromatic material with an orthochromatic filter, the contrast is insufficient and the two are not properly differentiated in the negative.

Since color contrast can be reproduced in monochrome only as differences in brightness, in the case of a subject of this nature contrast must be produced by darkening or lightening the tone in which one of the colors is reproduced in relation to the other. This may be accomplished by using a filter which absorbs more of one of the colors than the other. Consider the case of a tree with red apples. A green filter will render foliage lighter than the apples, while a red filter partially absorbing green will render the apples relatively lighter than the foliage. Consequently, to render a color *lighter* than it would appear with orthochromatic reproduction, a filter which selectively *transmits light* of the same color must be used, while to render a color *darker,* it must be photographed with a filter which *absorbs* light of the same color.

The proper filter to use under any given conditions depends upon the subject and involves a decision first as to what color, or colors, are to be rendered lighter (or darker) and second, the degree of contrast to be produced. As a general rule, the warm colors such as yellow, yellow-green, orange and red should be rendered as lighter than the cool colors such as violet, blue and blue-green. The extent to which a color should be lightened or darkened depends so much upon the subject and the results desired, that no definite rule can be given; judgment based upon experience is the only safe guide. Special filters, known as *viewing filters,* designed to show how the colors of a subject will be reproduced by a particular film or plate with different filters are helpful in choosing the proper filter for the effect desired The effect of a contrast filter may be determined simply by examining the subject through the filter. In using filters in this way, it is important not to be misled by color; one must learn rather to look for the effect of the filter on the *contrast* of different parts of the image.

Filters in Landscape Photography.—Among the chief uses of filters in landscape work are for the purpose of:

1. *Securing clouds in the sky and controlling the intensity of the sky.* With modern orthochromatic and panchromatic materials, only a comparatively light yellow filter is required to darken the sky sufficiently to bring out clouds with the proper contrast. The use of yellow contrast,

or minus blue filters, darken the sky considerably and increase the contrast between the clouds and the sky. Still greater contrast is obtained by using a red filter and panchromatic film or with infra-red material. Another application of filters is for the purpose of lowering the brightness of the sky so as to prevent excessive contrast when near dark objects are outlined against the sky.

In architectural photography, minus blue or orange-red filters are sometimes required when photographing white or light colored structures outlined against the sky to darken the sky and provide sufficient contrast between the buildings and the sky.

2. *To improve rendering of colors of foliage, flowers, etc.* Photographers have become so accustomed to the incorrect rendering of blue-sensitive material, that photographs which correctly portray the luminosities of the subject are often regarded as overcorrected. Grass and foliage is in general rendered too dark without filters and by not preserving the proper differences in color luminosities, the effect of aerial perspective is destroyed. With modern orthochromatic and panchromatic materials, only light filters are necessary. Care should be taken not to overcorrect through the use of filters which are too strong.

3. *To penetrate haze and secure sharp definition on distant objects.* The intervening haze which obscures distant objects is due largely to the scattering effect of particles of water vapor in the atmosphere. The scattering effect of these particles of water vapor, at a maximum in the ultraviolet, decreases progressively with longer wave lengths. Hence, the use of filters which absorb the ultra-violet and violet will result in an improvement in the definition on distant objects. With strong yellow, orange, or red filters, absorbing more and more of the light rays scattered by the particles of dust and water vapor, the definition of distant objects is greatly improved.

In landscape work, the total elimination of haze is not generally desirable as the recession of planes due to the effect of the atmosphere is destroyed and distant objects are made to appear too close to the camera. In mountain work and in telephotography, however, sharp-cutting yellow or orange-red filters are decidedly useful and in many cases absolutely necessary if satisfactory results are to be obtained. The lightest filter generally suitable for work of this kind is the minus blue; that is, a filter which absorbs ultra-violet, violet and blue. Greater

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Mees—Luminosity Filters. Brit. J. Phot. **53** (1906) 430.

Renwick—Color Values in Monochrome and a New Viewing Filter to Assist in Obtaining Them. Phot. J. **59** (1919) 158.

penetration of haze is obtainable with a strong yellow filter, such as the Wratten G, or an orange-red filter such as the Wratten A. For maximum penetration of haze, infra-red materials should be used with appropriate filters.

Filters in Portrait Photography.—Color filters are not generally used in portrait photography, partly perhaps on account of tradition, partly on account of the increased exposure required, and partly because of the general practice of retouching.

Flesh values are recorded satisfactorily with modern panchromatic materials without the need of a filter. Panchromatic materials having a high orange-red sensitivity tend towards the overcorrection of flesh values when exposed by clear tungsten illumination. To offset this tendency, blue-glass (photo blue) bulbs are frequently employed either alone or in combination with clear tungsten illumination.

Filters in Commercial Photography.—Filters are used in so many different ways in commercial photography that no general treatment of the subject is of much value In general, modern practice is to use filters on virtually every colored object except in cases where a satisfactory rendering is obtainable without a filter. Both orthochromatic and contrast filters are used depending upon the end in view. Generally, strict orthochromatic reproduction is regarded as important only if the print is to be colored or if the reproduction of the color differences of the original is of paramount importance. In the larger number of cases, the aim is to produce in the photograph the degree of contrast between the different colors which is regarded as suitable for that particular subject. However, a few examples may be useful. Panchromatic materials and contrast filters are virtually necessary in photographing furniture. It is almost impossible, for example, to secure a satisfactory rendering of red mahogany on an ordinary, blue-sensitive film or plate, or even on an orthochromatic material except with a lengthy exposure, but with a panchromatic material and a red filter, the grain of the wood is brought out so clearly as to be almost incredible. With yellow woods, such as oak, satinwood and walnut, like results will be obtained with a strong yellow filter. Tapestries and carpets require either orthochromatic or contrast filters as do colored posters, labels, colored maps, sepia-toned photographs, purple violet or blue typewriting (green filter), blue print (red filter), stained prints (filter the color of the stain), weathered brick buildings (strong yellow, orange, or even red filters).

Optical Properties of Light Filters.—Light filters are produced in one of three ways:

1. By dyeing thin sheets of gelatin with suitable dyes to produce a gelatin film filter which may be used alone or cemented between first quality glass for greater protection.
2. By infusing the molten glass or plastic during manufacture with suitable coloring materials.
3. By colored liquids contained in cells of glass or other suitable materials.

The first method is by far the most important. A large number of suitable dyes is available and filters having almost any desired absorption characteristics may be prepared. The gelatin film is easily damaged but this is avoided by cementing it between two pieces of glass. Filters produced in this manner are quite satisfactory if the cementing has been done properly and the glass is flat; the only drawback is that heat, moisture or excessive strain may cause the cement to soften, or give way, thus producing inequalities in the filter which affect its performance.

The number of colored substances which may be added to molten glass in the process of manufacture is rather limited and the production of colored glass filters has been hampered: (1) by the difficulty in finding substances having the required spectral absorption and (2) by the difficulty experienced in producing a uniform product. Recently, some success has been attained in the use of low temperature plastics in place of glass. Colored glass filters are rather more durable than those formed by cementing gelatin film between glass, but their absorption characteristics are not as well adapted to the requirements of modern color-sensitive materials.

Liquid filters are now seldom employed, except for special purposes, owing to their bulk, inconvenience and rapid deterioration.

Gelatin film filters, owing to their thinness, are practically without effect on the definition of the lens.

For ordinary purposes, filters prepared by cementing the gelatin film between carefully selected pieces of optical glass are satisfactory if the cementing is done carefully to avoid strains in the glass. To ensure satisfaction, however, only filters of the highest repute should be chosen. Cheap filters are poor economy; as filters, they are frequently ill adapted to the requirements of modern sensitive materials while the glasses used are neither plane nor parallel and the cementing faulty. With long focus and telephoto lenses and the large aperture lenses used on miniature cameras, it is especially important that only filters of the highest quality be used.

For three-color process work, filters cemented in optical flats and tested to work together must be used if three equal-sized images are to be obtained.

The filter may be placed in one of several positions:

1. *Over the light source.* This is the usual position in photomicrography and other branches of photography in which small light sources are used as in this position the filter cannot possibly affect the definition of the lens image.

2. *In front of the sensitive material.* This involves the use of larger filters than when used over the lens but is the most convenient method in repeating backs for making three-color negatives and in tri-color cameras.

3. *Between the lens combinations.* This position is possible only with gelatin film filters.

4. *Before the lens.* In general, this is the best position for the filter. In this position, it is more accessible and has the further advantage that any imperfections in the filter have less effect than if placed behind the lens. Moreover, the focal length of the lens, for all practical purposes, remains unchanged. This is obviously an important consideration when using a filter on cameras focused by scale.

5. *Behind the lens.* This position is less suitable than in front of the lens for the reasons mentioned above, and also because placing the filter behind the lens displaces the image by a distance which is approximately one-third of the thickness of the filter.

Care of Filters.—Because gelatin filters are easily marked, they should be handled as little as possible. The best way to use them is, when possible, to place the filter between the combination of the lens where it will be protected. Film filters may also be used in caps which slip on over the front of the lens, but exposure to moisture will in time cause them to cloud.

Cemented filters should receive the same careful attention as a lens. They should be kept clean by polishing them from time to time with a piece of lens tissue or silk. If necessary, a clean cloth moistened with alcohol may be used to clean the glass surface of a filter. In doing so, care should be taken not to allow the alcohol to reach the edges, as the cement may be softened, allowing air to enter. Cemented filters should be protected from heat because by its softening the balsam, a strain may be set up which may affect the definition of the lens with which the filter is used.

Most filters are quite stable to light; yet excessive exposure to strong light should be avoided.

Polarizing Screens.—While polarizing screens are not color filters and only affect the rendering of color indirectly, there is a similarity in that both are used to control the tone values of a photographic image. The term, polarized, as applied to light does not have reference to its color nor its intensity, but to another property which, unlike the other two, is invisible and has to do with the way in which a ray of light vibrates. Ordinarily, the rays of light from the sun, or a source of artificial light, such as a tungsten lamp, vibrate in all directions at right angles to the ray itself. When the ray of light is polarized, however, the vibrations in all but one direction are cut out. A ray of light which is polarized will pass through a polarizing body if the vibration of the ray is in line with the vibration plane of the body, but is absorbed more and more as the screen is rotated away from this position.[5]

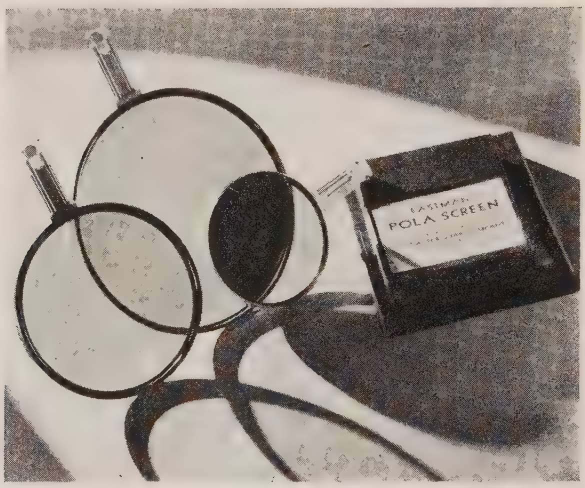

Fig. 278. Polarizing Screens (Pola-Screens) for Use Over the Lens. The Polarizing Planes of the two screens at the left are parallel while those of the two at the right are at right angles (crossed to one another).

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[5] For a detailed explanation of polarization, see any standard text book on light, as, for example, Barton, *A Textbook on Light.* Longmans (New York, 1939).

Polarizing materials have been known for years but not until the introduction of *Polaroid* by Land[6] was it possible to obtain such material in a form suitable for photographic use and at a reasonable price. Polaroid combines a polarizing material in the form of minute-rod-like crystals parallel to one another, imbedded in a sheet of plastic. For photographic use, the sheet material is cemented between glass plates. Two types of polarizing screens are now available for photographic purposes; one for general use over the lens, the other for use over the light source.

Light which is polarized in one plane is fairly common; for example, light from a clear blue sky at a right angle to the sun's rays is strongly polarized, and when this sky light is reflected from water, the reflected light is also polarized. In addition, light specularly reflected from any non-metallic surface at an angle of approximately 32° to the surface is strongly polarized by the reflection. A lesser amount of polarization is produced at other angles of reflection, and none at zero or at an angle of 90°.

Polarizing screens over the lens alone are useful for:

1. *Controlling the brightness of the sky.* A polarizing screen placed over the lens enables the brightness of a clear blue sky to be darkened as desired simply by rotating the screen until the effect desired is obtained. The use of polarizing screens for controlling the brightness of the sky has the advantage over filters in that (1) the color rendering of the objects in the foreground is not altered, (2) filters may be used independently to secure the desired effect in the forground, and (3) the effect produced by the polarizing screen is easily determined from the appearance of the image on the ground glass or in the finder.

Polarizing screens, however, are ineffective when photographing against the sun or directly away from it, or when the sky is overcast. The maximum effect is obtained when the sun is to one side of the camera at a right angle to the optical axis of the lens.

2. *Control of Contrast.* The use of polarizing screens makes it possible with certain subjects to control the relative brightnesses of different parts of the image without changing the lighting. Among the subjects offering such possibilities are the walls and roofs of buildings, sunlit water, wet pavements, etc.

3. *Photographing through glass or water and to control reflections.* Reflections from glass, water, linoleum, polished woods, glass tile,

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[6] Land, U.S.P. 1,918,848; 1,951,664; 1,956,867; 1,989,371.

painted and lacquered surfaces, leather, fabric and other non-metallic reflecting surfaces can be removed to show detail beneath by the use of a polarizing screen over the lens if the camera angle and the illumination are at an angle of approximately 30° to the surface. At other angles, the reflections may be partially but not entirely removed except at an angle of 90° when the polarizing screen is ineffective.

4. *As a neutral density filter.* Two polarizing screens used together in front of the lens form a variable neutral density filter with a density range of from 0.5 to 2.8 (transmission 32% to 0.16%).

The use of a polarizing screen over the lens necessitates an increase in exposure of approximately four times with panchromatic and six times with orthochromatic material, but this exposure factor is the same for all positions of the screen.

When the light reaching the subject is polarized by means of polarizing screens placed over the light sources and a second polarizing screen is placed over the lens, the position of the camera and light source is not limited to a single effective angle as is the case when a single polarizing screen is used over the lens. Thus, by using polarizing screens over both the light sources and the lens, the commercial photographer is enabled to eliminate or at least greatly subdue troublesome reflections when photographing such subjects as oil paintings, carved and polished wood, lacquered surfaces, articles in transparent wrappings, glass, clinical specimens, in copying photographs on rough-luster papers, etc. The exposure is increased considerably but in most cases this is of no consequence.

McFarlane and Tuttle—Photographic Possibilities of Polarized Light. J. Soc. Mot. Pict. Eng. **25** (1935) 69.

McFarlane—Demonstration of Photography by Polarized Light. J. Soc. Mot. Pict. Eng. **26** (1936) 679.

CHAPTER XVI

NEGATIVE MATERIALS

In this chapter, negative materials will be discussed first from the standpoint of the support on which the sensitive emulsion is coated, namely, glass plates, film and paper, then from the standpoint of color sensitivity, after which the choice of negative materials for different purposes, specialized negative materials and the storage of sensitive products will receive consideration.

Glass Plates.—Glass has been used as a support for light sensitive layers since the earliest days of photography, and not until the introduction of the nitrocellulose film base in 1889 was its supremacy questioned. Today, glass plates have largely been superseded by film, but in certain specialized fields of photography in which the dimensional accuracy of the image is an important factor, as in spectrography, astronomy, in half-tone photo-engraving, glass plates are still employed.

Glass for photographic purposes must be clear, free from color, bubbles, striae and other imperfections and reasonably flat. Its thickness must, in general, increase with the size of the plates. For certain purposes, such as spectrography, light weight glass with a high degree of flexibility must be used, as the plate must be bent to fit the exposure plane of the holder in order to secure a sharp image of the spectrum. Small plates must usually be on thin glass to adapt them to the thin metal plate holders used in small cameras. On the other hand, the large plates required in photo-engraving are coated on heavy glass to prevent curving in the holder, which would affect the defintion of the half-tone image.

In any case, an emulsion coated directly on glass has a tendency to frill when wet or to strip off when dry. The surface of the glass, therefore, must first be treated to obtain good adhesion of the emulsion layer. Glass plates are commonly given a substratum consisting of a thin coating of gelatin strongly hardened by chrome alum or a chemical etching method may be employed.

Glass plates are coated with emulsion by a machine (Fig. 279) which spreads a thin and uniform layer of emulsion over the glass plates as they are conducted past the coating apparatus on a moving belt. Several coating devices have been described in the literature. In one of the earliest machines the emulsion simply flows over the lips of a long, narrow trough onto the glass plate. The emulsion must, of course, be kept at a suitable temperature in order that it may flow readily. In another machine described by Cadett, the arrangement is very similar except that directly behind the trough from which the emulsion issues is a light-weight roller which acts as a spreader and smooths out the layer of emulsion on the plates. In still another machine, described by B. J. Edwards, the emulsion was contained in a long trough the width of the glass to be coated. In this trough a glass cylinder is revolved. A scraper, or squeegee, on one side of the cylinder removes the emulsion carried around the cylinder and allows it to drain down onto the glass plate.[1]

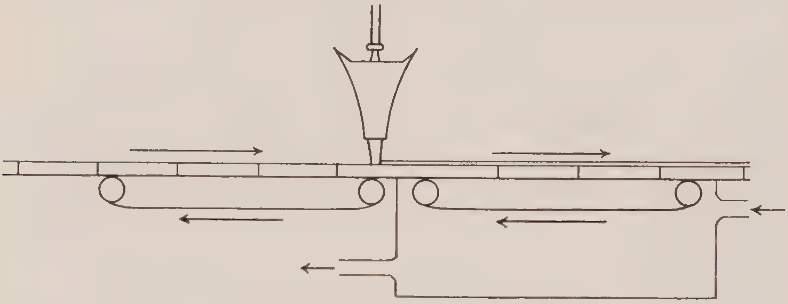

Fig. 279. Diagram Showing Principle of Plate Coating Machine. (From Baines, *British Journal of Photography.*)

After being coated with the emulsion, the plates are carried on a movable belt through a cold chamber or compartment in which the emulsion is chilled and set to a gel. Upon reaching the end of the conveyor system, the plates are removed and dried under controlled conditions.

Glass plates are ordinarily packed in boxes of one dozen with the emulsion sides facing in pairs. In America, plates are usually packed in three-part boxes for added protection, while British and foreign plates are generally packed in a box with a single cover and the box enclosed in a sealed paper wrapper. The emulsion side of glass plates may be identified by the reflection of the safelight in the glass side or, when loading holders in darkness, by remembering that the odd-numbered plates face emulsion side down and the even numbers face up, or by slightly moistening the lips and applying to one corner of the plate. The lips will adhere slightly to the coated side.

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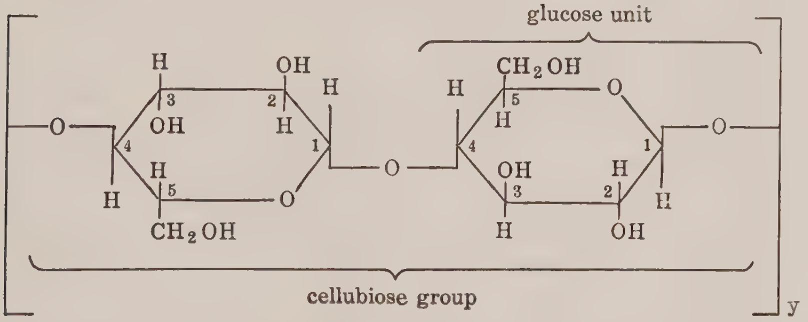
[1] Smith, *Eder's Jahrbuch,* 1892, p. 385; Cadett, B.P. 9,886 of 1886, and 13,725 of 1887; Edwards, *Phot. News* 1884, p. 541.

Film, The Base.—When cellulose in the form of cotton linters or wood pulp is treated with nitric acid or acetic anhydride in the presence of suitable catalysts, or dehydrating agents, cellulose nitrate or cellulose acetate is formed.

The purer forms of cellulose have an empirical composition which corresponds to $(C_6H_{10}O_5)_x$. Chemists have shown by combined acetylation and hydrolysis that cotton forms the octacetate of cellobiose, a dissacharide composed of two glucose units. The cellulose molecule consists of long chain of glucose units which are linked together by 1-4-glycosidic oxygen bonds. According to Haworth,[2] the formula for cellulose is:



Staudinger[3] found that the degree of polymerization of cotton, as glucose units, is approximately 750 and since each glucose unit has a combined atomic weight of 162 the molecular weight for cotton cellulose is in the order of 120,000. Polymerization values for other celluloses reported by various investigators range from 10 to 3000, indicating particle weights of 1600 to 450,000.

It should be noted that the cellulose molecule is made up of glucose units and that each unit contains three OH, hydroxyl groups, which may become involved in esterification.

[2] Haworth, *J Soc. Dyers and Colorists* 50, Jublilee issue.

[3] Staudinger and Jurish, *Kunstseide* (1) 21 (1939) 6–9.

SUTERMEISTER—The Chemistry of Pulp and Paper Making. Wiley (1941) pp. 11–19.

GILMAN—Organic Chemistry—An Advanced Treatise, Vol. II. Wiley (1938) pp. 1535–1583.

Esterified cellulose may exist in two forms: (1) fibrous, in which the form of the fiber is retained and (2) dope, in which the surface of the fiber dissolves as esterified and forms a solution.

Cellulose Nitrate.—If cellulose is treated with nitric acid, cellulose nitrate and water are formed. Since the presence of water causes the reaction to be reversible it is necessary to introduce a strong dehydrating agent, as sulfuric acid.

$$\underset{\text{Glucose Unit}}{(C_6H_7O_2(OH)_3)_x} + 3xHNO_3 \rightleftarrows (C_6H_7O_2(NO_3)_3)_x + 3xH_2O$$

In dealing with reactions of cellulose, one does not consider the entire molecule but speaks in terms of single glucose unit. Nitration is *complete* if there are three nitrate groups per glucose unit and *partial* if the average number of nitrate groups per unit is less than three. Based on the percent of nitrogen per glucose unit, cellulose nitrates may be considered to be mono, di, or tri nitrates if they contain 6.77, 11.13, or 14.16% nitrogen, respectively.

Properties of cellulose nitrate vary with the cellulose used and with conditions of nitration. Chain lengths for cellulose nitrate range from 200 to 3000 glucose units. The solubility depends on the degree of nitration. Viscosity of nitrate solutions varies with both the source of cellulose and the conditions of nitration. The relation between the degree of polymerization of original cellulose and that of the final product is important.

Cellulose containing two and a fraction nitrate groups per glucose unit, 11 to 12.4% nitrogen, is known as pyroxylin and because of its solubility, flow, adhesion, and compatibility with suitable solvents is used for manufacture of film base.

Amor [4] gives as a typical nitrating mixture:

60% sulfuric acid
20% nitric acid
20% water.

The cotton linters are nitrated at 40° C. for 20 minutes under conditions of constant agitation. The resulting product is washed, neutralized and

[4] Amor, *Phot. J.* **78** (1938) 459.

Sheppard and Newsome—Film Formation with Cellulose Derivatives. J. Soc. Chem. Ind. **56** (1937) 1.

Sheppard—The Removal of Free Acid from Nitrocellulose. J. Ind. Eng. Chem. **13** (1921) 1017.

bleached. For safety in storage, cellulose nitrate is moistened with alcohol and kept in metal drums.

Cellulose Acetate.—As organic acids do not react satisfactorily with cellulose, organic esters of cellulose are prepared commercially by treating the cellulose with a mixture of an acid anhydride, as esterifying agent; an organic acid, as diluent; and an inorganic acid, as catalyst. Cellulose acetate is produced by treating cotton linters with a mixture of acetic anhydride, glacial acetic acid and a catalyst, as sulfuric acid.

$$(C_6H_7O_2(OH)_3)_x + 3_x(CH_3CO)_2O \rightleftarrows (C_6H_7O_2(OCOCH_3)_3)_x + 3_xCH_3COOH.$$

By partially hydrolysing the triacetate first formed, with acetic acid and water, a product is obtained which contains 35 to 40% acetyl, or two and a fraction acetyl groups per glucose unit. This product was found by Miles to dissolve in acetone and form stable films on evaporation.

Important steps in the manufacture of the acetate are: acetylation, hydrolysis, precipitation in water, neutralization, washing, centrifuging and drying.

Because of its slow rate of burning, cellulose acetate is used in manufacture of the so-called "safety film."

Photographic film base is made by combining the cellulose ester or esters with suitable solvents, a plasticizer, and stabilizers. The function of the solvents is to dissolve the ester and permit a thin layer to form and dry. The addition of the plasticizer ensures flexibility and elasticity.

Films are formed from the cellulose ester solutions or "dope": (1) by allowing the solvent to evaporate, or (2) by coagulation with a non-solvent that is miscible with solvents used. Solutions used for coating are concentrated and very viscous. They are allowed to flow to a limited degree. Actual thickness is governed by means of scraper or "doctor."

The base is usually cast by spreading the dope in a uniform layer on a large heated chromium faced drum which rotates slowly allowing the solvent to evaporate and the base to dry sufficiently so that it can be scrapped off in a continuous sheet before the drum has made a com-

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SCHLOTTER—The Chemistry, Manufacture and Uses of Nitrocellulose. Chem. Met. Eng. **25** (1921) 281.

WORDEN—Technology of Cellulose Ester. Van Nostrand (1921) Vol. VIII pp. 2553, 2567.

plete revolution. The base is dried and then wound into rolls up to 60 inches wide and 2000 feet long. Actual thicknesses of film base are:[5]

Roll film	85 microns *
Motion picture film	140 microns *
Cut film	200 microns *

Important properties of the finished base are: transparency, flexibility, elasticity, tensile strength, thickness, moisture adsorption, low inflammability and freedom from specks.

Two types of film base are manufactured: cellulose nitrate and safety base. The latter is made from cellulose acetate, cellulose acetate propionate, cellulose acetate butyrate and in certain cases viscose.

Cellulose Nitrate Film.—The base is prepared from nitrated cotton containing 11 to 12.4% nitrogen. The ester used must be stable and readily soluble in suitable solvents.

Nitrate film dope is made by dissolving the nitrated cotton in a mixture of solvents, as methyl, ethyl or butyl alcohol, ether, acetone, ethyl or amyl acetate. A plasticizer like triphenyl phosphate or camphor is added. The amount of plasticizer used varies but for camphor it is usually 5 to 15% of the weight of cellulose nitrate. After filtering, the dope is ready for coating.

Formulas for the composition of film base are secrets among the manufacturers. However, Reviere and Clément[6] give the following formula for coating on a rotating drum:

Cellulose nitrate	17.75%
Acetone	88.00%
Amyl alcohol	1.00%
Camphor	3.25%

Castor oil may be added in an amount not to exceed 5% of the nitrate.

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[5] Parker, *Handbook of Photography.* McGraw-Hill (1939) Ch. IV p. 123.

[6] Clément and Reviere, *La Cellulose et les Ethers Cellulosiques,* Paris et Liege (1936).

Clark—In Thorpe's Dictionary of Applied Chemistry. Longmans, New York, 4th ed. (1938) Vol. II, pp. 446–456.

Wentzel.—Die Photographische, Chemische Industrie. Theodor Steinkoff, Dresden (1926) p. 91.

Theisen—The History of Nitrocellulose as a Film Base. J. Soc. Mot. Pict. Eng. **20** (1933) 259.

Didiée—Raw Film and Its Constituents. Tech. Cinemat. **8** (1936) 775; **9** (1937) 831.

Blonski—Various Methods for the Production of Film Base. Photo-Kino. Ind. **1** (1934) 72.

Safety Base.—According to Hageborn and Ossenbrunner,[7] an acetate film dope may be prepared by dissolving cellulose acetate containing 52.4 to 56% acetic acid in a mixture of chloroform, acetone, acetylene tetrachloride or methylene chloride and a plasticizer as dibutyl, tricresyl or triphenyl phosphate.

Ulman[8] gives the formula for a dope which contains 12 to 16% cellulose acetate and a plasticizer as triphenyl phosphate equal to 40% of the acetate. Acetone is preferred as the solvent, although other solvents as methyl acetate, methyl formate, amyl and ethyl acetates, chlorinated hydrocarbons, and di-acetone alcohol may be used.

Nitroacetate Safety Film.—If the nitrate content of a film base is reduced, the danger of explosion by ignition is lessened and the rate of burning is decreased. Safety films which are non-inflammable have been prepared by two methods: (1) Denitration of cellulose nitrate—by replacing part of the nitrate with acetate or acetyl groups; (2) The use of mixtures of cellulose acetate and cellulose nitrate.[9, 10] Films made by the first method have not been particularly successful industrially. Films obtained by mixing the two cellulose esters have better technical qualities and greater mechanical resistance than those containing only cellulose acetate.

Goldman and Sherman[11] have shown that the rate of burning of a cellulose film base is a linear function of the cellulose nitrate content and is also influenced by nature of the plasticizer used. According to their claims, nitroacetate films containing 20 to 30% cellulose nitrate and a phosphate plasticizer are *safe.*

Non-Deforming Film.—Film used for aerial photography should not deform, change in dimensions, when subjected to changes in temperature and humidity.

With the introduction of acetate film about thirty years ago, cellulose nitrate film has been gradually replaced with cellulose acetate. Disadvantages of early acetate film were: low tensile strength, greater brittleness under dry conditions, and a greater susceptibility to moisture. Distortion with humidity changes was the chief objection to the use of acetate film for aerial topographic mapping. The advantages of acetate film over nitrate film are low fire hazard, and greater stability under ordinary conditions of storage. Intense study on the methods and control in manufacture has made possible the production of acetate film which on the basis of shinkage and distortion is as satisfactory as nitrate. The susceptibility of aero safety film for water is no greater than that of aero nitrate film. It shows the same degree of uniaxialism.[12]

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[7] Hageborn and Ossenbrunner, U.S.P. 2,071,462.

[8] Ulman, Azetyl Zellulose, *Folien und Filme,* Halle (Saale) 1932.

[9] Goldman, *Soviet Kino Photo Ind.* **4** (1936) 35.

[10] Kodak Pathe, F.P. 834,554 (11–24–38).

[11] Goldman and Sherman, *Photo. Kino. Chem. Ind.* **6** (1935).

Charriou and Vallette[13] claim to have produced non-deforming films with a base of cellulose triacetate containing 60% acetic acid with 25% triphenyl phosphate dissolved in methylene chloride and ethyl alcohol. They state that the linear dimensions of a gelatin coated support, even after soaking for some time, did not exceed 0.015%.

Substratum Coating.—As emulsion will not adhere to film base, subcoating is necessary to prevent frilling of the gelatin layer when wet, or stripping when dry. Since hardened gelatin, as used for glass plates, does not adhere to film base, it is necessary to use a mixture of gelatin with an organic solvent of film base, such as acetone, ethyl acetate or an alcohol-ether mixture. Gelatin is insoluble in these organic solvents and the base is insoluble in water, but it is possible to prepare solutions consisting of gelatin and cellulose nitrate, or acetate, dissolved in a mixture of one of the organic solvents and water. The film base is coated with a thin layer of this and then dried. During drying, the organic solvents and water evaporate, depositing on the film base a surface layer of gelatin and cellulose nitrate or acetate. The cellulose nitrate deposited results in good adhesion of the substratum coating to the film base, while the gelatin present ensures good adhesion of the emulsion.

Film Coating.—Film base is coated with emulsion in rolls varying in width from 36 to 45 inches, and in lengths of 1000 feet or more. The principle employed is to pass the film base underneath a roller through the emulsion which is contained in a long shallow trough heated to the proper temperature to maintain the emulsion at the proper consistency for coating (Fig. 280).

[12] Carver, *Photogram. Eng.* **4** (1938) 223–225.

[13] Charriou and Vallette, *Phot. J.* **74** (1936) 31.

Fuchs—Preliminary Preparation of Photographic Layers. Phot. Ind. **34** (1936) 552, 554.

Charriou and Valette—Adhesion of Photographic Emulsion to Cellulose Acetate Supports. Sci. et. Ind. Phot. (2) **8** (1937) 99.

Kozloff—Mechanism of Adhesion of the Emulsion to the Support. Proc. International Congress of Photography, 1935.

Use of Synthetic Resins, see B.P. 470, 565 and B.P. 478, 357.

The quantity of emulsion applied per unit of surface is very important, since the coating weight affects the photographic quality of the sensitive material. Not only is it essential that the coating be of the proper thickness, but it must be uniform over both the width and the length of the roll and from one roll of base to another. Coating weight depends on several factors, chiefly the speed of the machine and the viscosity of the emulsion, and must be carefully watched.

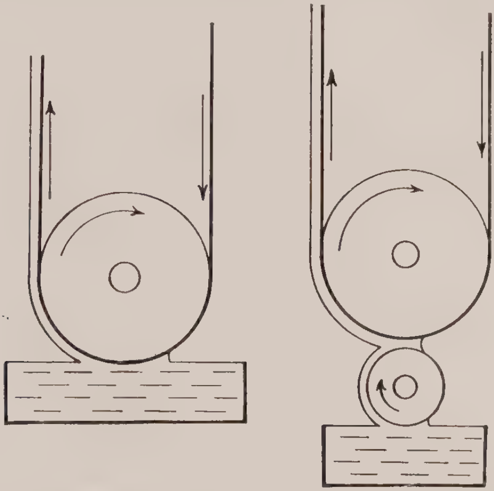

Fig. 280. Diagram Illustrating Principle of Trough and Doctor-Roller Coating Machine Use for Coating Film Base and Paper. (Baines, *British Journal of Photography.*)

From the coating machine, the film is conducted over chilled drums, or through a "chill box" containing refrigerated air, in which the emulsion sets to a gel. The band of film is then conducted by automatic machinery to the drying room where, moving constantly in loops, it is dried by clean air of the proper temperature and relative humidity. Drying is a very important operation as lack of uniformity in drying results in a variation in sensitiveness, while improper drying conditions may seriously affect the quality of the product in other ways.

Special Coatings.—Film base, which has a high degree of flexibility, curls badly as the emulsion dries because of the contraction of the gelatin. This curling is counteracted by treating the opposite side of the base so as to cause it to contract equally, but in the opposite direction. In roll film and sheet film, this so-called *non-curl coating* usually consists of gelatin while in motion picture film the back of the film is treated with solutions of certain cellulose esters which have the same effect, and in some cases, tend to reduce the liability of static electrical discharges upon the unwinding of the roll.

On sheet and roll film, dyes which absorb light but are decolorized by the processing solutions, may be added to the gelatin coating applied to the rear of the film base to produce a *non-halation backing.* In motion picture film, where a dye backing would be objectionable, non-halation properties are obtained by the addition of suitable light absorbing material to the film base itself producing what is termed, *gray base film.*

If a sensitized surface, whether film, paper or glass plate, is subjected to surface friction, or abrasion, the portions affected by the stress are made developable, or in some cases, partially desensitized. This is a surface effect which can be prevented in a considerable degree by applying a thin layer of gelatin over the emulsion, the protective or *super-coating* forming what is sometimes called a *non-abrasion* layer or coating.[14]

Sheet or Cut Film.—Sensitized film in cut sizes for use in film holders or in plate holders with film septums is termed *sheet film* or *cut film* and has largely replaced glass plates. The thickness of the base is usually several times as great as for roll or other film, to reduce curling and maintain flatness in the usual form of holder. Sheet film is usually packed in boxes of one dozen with the emulsion sides all facing the same way, the films being separated from one another by sheets of black paper. The American practice is to indicate the emulsion side and the type of film by notches in one side of the sheets. These are placed so as to be in the upper right hand corner when the emulsion side faces the observer. The number and shape of the notches indicate the type of film.

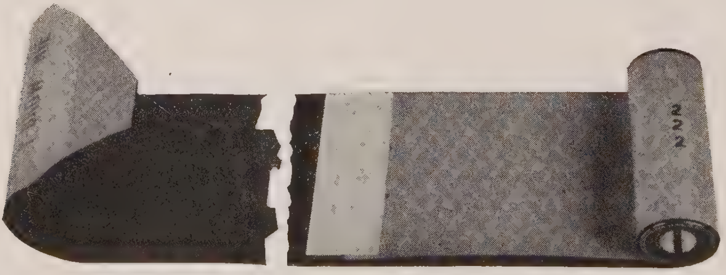

Fig. 281. Spooling of Daylight Loading Roll Film.

[14] B.P. 450,220 of 1936.

Roll Film.—The manner in which roll film is made daylight loading is shown in Fig. 281. The strip of film is attached at one end with an adhesive sticker to a long strip of opaque paper. Then, when the film is wrapped around the spool, the end of the paper strip protruding beyond the film protects the film from light so that it may be placed in the camera in daylight. The strip of paper extending beyond the other end of the film strip operates in the same way to permit removal of the film from the camera in daylight.

Film Pack.—The principle of the film pack is shown in Fig. 282. Twelve cut films each attached to an opaque black paper tab are placed in a metal or cardboard container. The ends of the paper tabs project from the top of the pack and by pulling out the tab the film is transferred from its position at the front of the pack to the rear section. In front of the pack is an opaque black paper "safety cover" which protects the films from light until the pack is placed in the camera, or in the light-tight adapter. This safety cover is transferred to the rear of the pack by pulling out the safety tab before the first exposure is made. When the last exposure is made, the pack is rendered light-tight by the center partition which is now in front in the position occupied in the beginning by the safety cover.

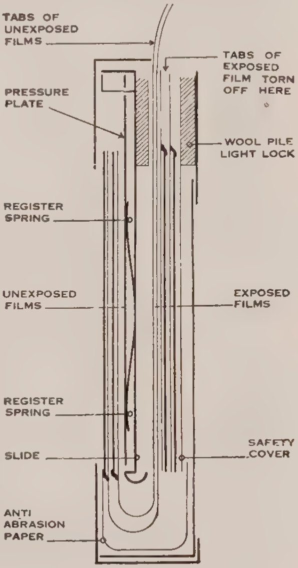

Fig. 282. Drawing of Cross-Section of Film Pack Showing Construction.

Cartridge Film.—Perforated 35 mm. roll film is ordinarily supplied for use in miniature cameras enclosed in daylight loading metal cartridges consisting of an inner spool and an outer container or cartridge (Fig. 283). The film transport mechanism of the camera is threaded with the strip of

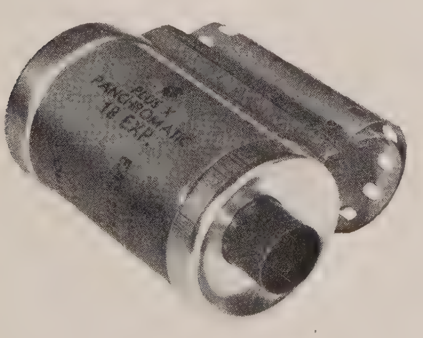

Fig. 283. Film Cartridge for 35 mm. Film for Use in Miniature Cameras.

film projecting from the cartridge and the camera closed. With each successive exposure, the film is drawn through the narrow slit in the side of the cartridge and wound up on the take-up spool within the camera. When the last exposure has been made, the film transport mechanism is reversed and the film wound back into the cartridge container which may be removed from the camera in daylight.

Paper.—Paper is used as an emulsion support chiefly for positive rather than negative materials. As far as the latter are concerned, the use of paper as a support is confined almost exclusively to (1) photocopying papers of the type used in the *Photostat, Rectigraph* and similar equipment, (2) as a base for emulsion layers which, after processing, are stripped from the support and transferred to glass (strip film for lithography and other graphic arts processes) and lastly, (3) direct positive materials in which the negative image is reversed to a positive in processing. These specialized materials will be discussed under that heading later in this chapter.

The paper base employed for such purposes is invariably made especially for photographic purposes. Among the major requirements are a high degree of freedom from all foreign substances which would affect the emulsion and physical strength to withstand the various processing baths. Some of these are acid, some alkaline and the paper stock must have the physical strength to withstand these changes as well as the temperature changes, prolonged washing and handling which photographic papers ordinarily receive in practice.

The paper is usually coated or "sized" before the emulsion is applied. This coating may consist of hardened gelatin or baryta-barium sulfate in gelatin. The purpose of such coatings is to ensure satisfactory adhesion of the emulsion and to act as an insulating layer between the paper base and the emulsion preventing too great an absorption of the emulsion by the paper stock.

Types of Color Sensitive Materials.—The variation in sensitivity with the wave length of the radiation to which the film, or plate, is exposed is termed spectral or *color* sensitivity. There is a wide variation among negative materials in this respect; however, it is usual to consider all photographic materials designed for use in the visible region as belonging to one of three classes: (1) *ordinary,* or blue-sensitive, (2) *orthochromatic,* or less frequently, *isochromatic* and (3) *panchromatic.*

1. *Blue-sensitive Materials.* The spectral sensitivity of materials of this class ends for practical purposes at a wave length of approximately 500 millimicrons. Materials of this type, therefore, respond only to

violet and blue, and are practically insensitive to such visually brilliant colors as green, yellow, orange and red. In this class belong all films and plates which are not rendered sensitive to radiation of longer wave lengths through the addition of a sensitizing dye. (Chapter VII.) This includes all developing papers, lantern slides and transparency plates and films and some negative materials.

2. *Orthochromatic and Isochromatic Materials.* Photographic materials sensitive to yellow as well as to violet and blue are termed *orthochromatic,* i.e., true color, or *isochromatic,* i.e., equal color. Orthochromatic or isochromatic plates and films are practically insensitive to radiation of wave lengths longer than 600 millimicrons; they do not respond, therefore, to spectral orange or red. However, since most natural reds reflect some green and yellow, red is rendered lighter than with a blue-sensitive material.

In Fig. 284 is shown the spectrogram of an orthochromatic material sensitized with erythrosin (see p. 250). Erythrosin was used widely as a sensitizer for orthochromatic materials until a few years ago, so that the spectrogram shown may be regarded as fairly representative of the older orthochromatic films and plates on the market.

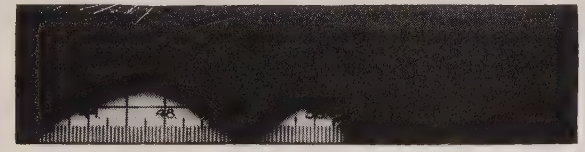

FIG. 284. Wedge Spectrogram of Orthochromatic Material Sensitized with Erythrosin.

The discovery within recent years of more efficient sensitizing dyes has made possible orthochromatic materials with a higher green and yellow sensitivity than were possible with erythrosin. Some of these are shown in Fig. 285. It will be noted that with the newer dyes not only has the sensitivity to green and yellow been increased, over that obtained with erythrosin, but that the depression near a wave length of 550 millimicrons has almost completely disappeared.

3. *Panchromatic Materials.* Until about 1925, the dye most commonly used for panchromatic materials was pinacyanol (Fig. 286). Few such materials are now available commercially, having been superseded by new films and plates employing the more efficient sensitizing

dyes which have been discovered since that time (see Chapter VII). There is considerable diversity in present day panchromatic materials, both with respect to color sensitivity distribution and the variation in gamma with the wave length region used for the exposure. This variation in contrast when filters are used, while of particular importance in three color photography, is sufficiently marked in some cases to be of some concern in ordinary photography. There are, however, practically no specific data on this subject so far as commercial panchromatic films and plates are concerned.

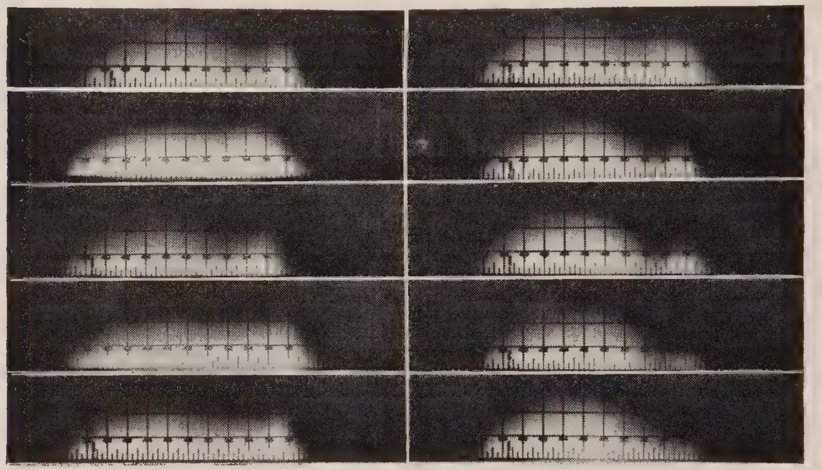

Fig. 285. Wedge Spectrograms of Typical Orthochromatic Materials.

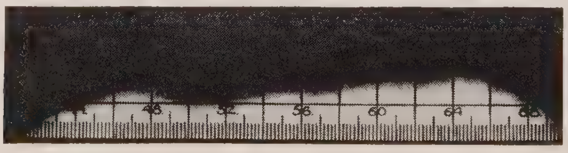

Fig. 286. Wedge Spectogram of Panchromatic Material Sensitized with Pinacyanol.

Wedge spectrograms illustrating the distribution of color sensitivity for several typical panchromatic materials are shown in Fig. 287. Attention is again called to the fact that, while useful for comparative purposes, wedge spectrograms should not be accepted as representing the actual distribution of sensitivity with wave length and may lead to erroneous assumptions respecting sensitivity, unless consideration is given to the conditions discussed on p. 438.

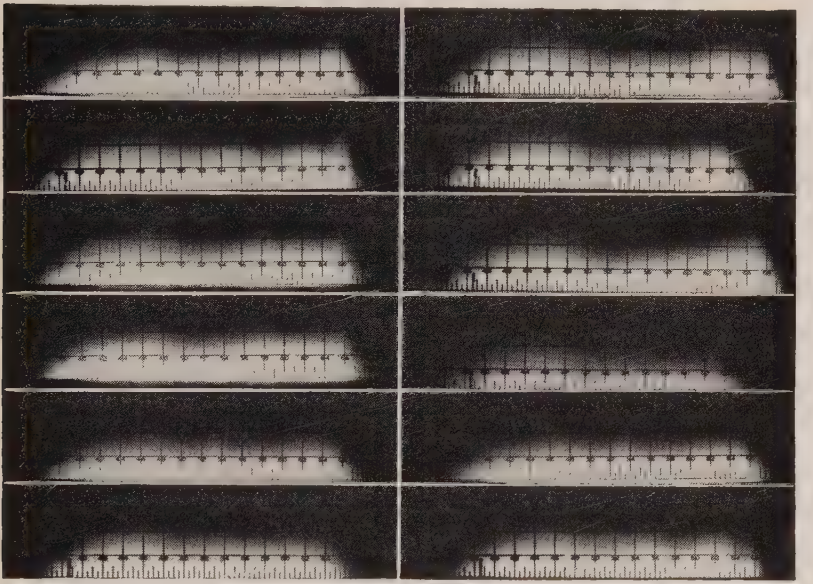

Fig. 287. Wedge Spectrograms of Typical Panchromatic Materials.

Factors Affecting the Choice of a Sensitive Material.—Some of the considerations involved in the selection of a negative material for a specific purpose are outlined below. The order of importance naturally varies with the use made of the sensitive material.[15]

1. The permissible time of exposure; i.e., the speed of the material.
2. The requirements of the subject as respects the rendering of color; i.e., color sensitivity.
3. The degree of contrast required in the negative; i.e., maximum useful or readily attainable gamma.
4. The sharpness required of the image; i.e., image sharpness, resolving power, halation.
5. Time required in processing. Important in press photography and certain other fields.

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[15] Color photography constitutes a special case and will be discussed later.

6. Ability to withstand processing solutions at a relatively high temperature; i.e., freedom from frilling, softening, etc.

7. Graininess of the developed image. Graininess varies with developing conditions but is an important emulsion characteristic.

8. Useful exposure range; i.e., the ability to properly reproduce a subject with an extended brightness range and an important factor in exposure tolerance.

Sensitive Materials for Portraiture.—Sensitive materials for portraiture must have a long scale of gradation, high speed, reasonably fine grain and medium contrast.

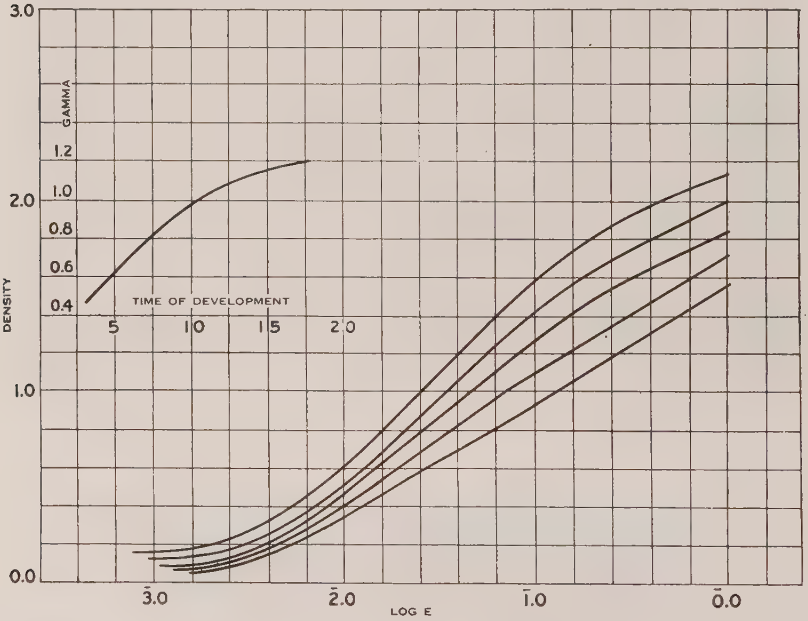
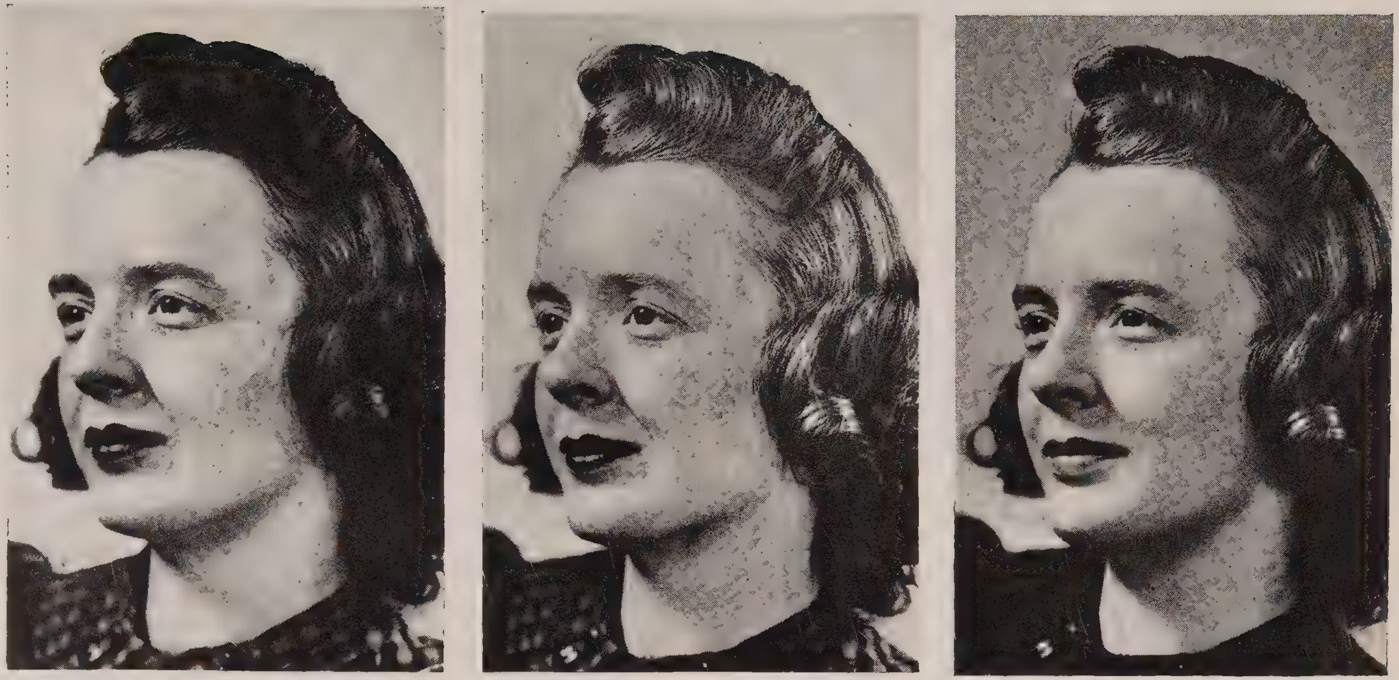


Fig. 288. *D* log *E* and Time-Gamma Curves of a Negative Material Designed for Portrait Photography.

The sensitometric characteristics of a typical negative material for studio portraiture are shown in Fig. 288. Both ordinary (blue-sensitive) orthochromatic and panchromatic materials are in use but color sensitive materials are to be preferred because of the superior rendering of flesh values (which eliminates a large amount of the retouching necessary with blue-sensitive materials), the improved color rendering of the hair, eyes, lips and dress colors and lastly the higher speed when arti-



(*A*) (*B*) (*C*)

Fig. 289. Photographs of a Subject with a Freckled Skin Photographed. (*A*) on a Blue-sensitive Material, (*B*) an Orthochromatic Material, and (*C*) a Panchromatic Material.

ficial light is employed. High speed orthochromatic materials are preferred by many especially when clear tungsten lamps are employed as producing better rendering of skin textures than panchromatic materials and permitting development by a red safelight.

Panchromatic materials are widely employed, however, both with photoblue and clear tungsten lamps, electric arcs as well as with daylight. In Fig. 289 are shown comparative photographs of a typical portrait subject on blue-sensitive, high speed orthochromatic, and orthopanchromatic materials with incandescent clear tungsten illumination.

Sensitive Materials for Press Work.—Films and plates for press work must be of high speed, for much press work must be done under unfavorable light conditions, should develop rapidly and produce contrast readily, have a fine grain and be physically hard, to withstand forced processing and drying.

The sensitometric characteristics of a typical high speed negative material, designed particularly for press photography, are shown in Fig. 290.

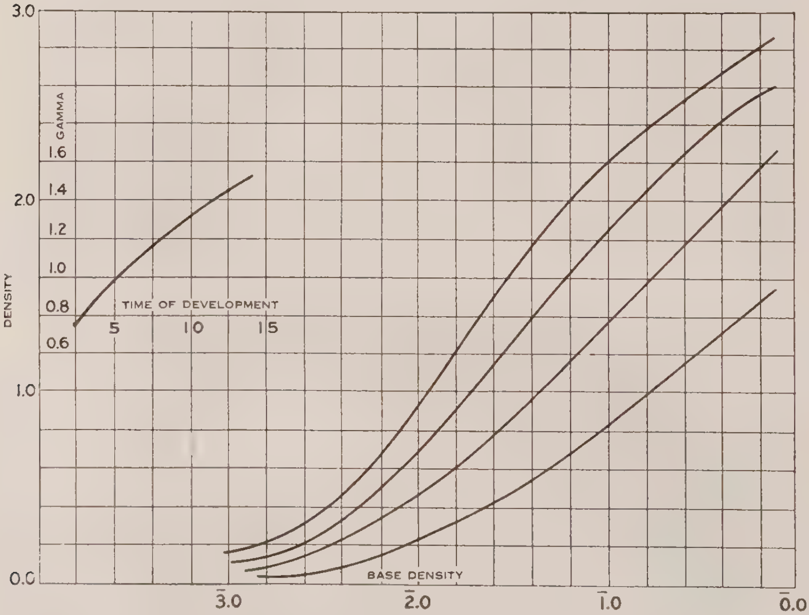


Fig. 290. *D* log *E* and Time-Gamma Curve of a Negative Material Designed for Press Photography.

Both ordinary (blue-sensitive) orthochromatic and panchromatic materials are in general use with the tendency towards the last mentioned due to its greater speed with tungsten illumination. Both plates and sheet film are in general use although it would appear that glass plates will in time be superseded by film on account of its lesser weight, freedom from breakage and general convenience.

Materials for Landscape Photography.—In general, color sensitive materials are preferred for landscape photography although for the atmospheric effects of early morning or late afternoon, ordinary (blue-sensitive) materials are favored by some as emphasizing the atmospheric effect. However, if the proper rendition of the colors of the subject or of clouds, is desirable, color sensitive materials are a necessity. Since brilliant reds are rare in the average landscape, orthochromatic materials are suitable although equally satisfactory results are obtainable on panchromatic materials with lighter filters and usually with less exposure.

For distant views, mountains, scenery, and in aerial photography, panchromatic materials with a strong yellow, orange-red or red filter are required (p. 467). Still greater penetration of haze is obtained through the use of infra-red sensitive materials and suitable filters.

Sensitive Materials for Commercial Photography.—Commercial photography covers an exceedingly wide range of subjects and no one type of sensitive material is suitable for all.

For illustrative work with models, panchromatic materials of high speed and brilliant gradation of the types shown in Fig. 288 and Fig. 290 are preferred by most photographers. Materials of this character are also favored for interiors, show windows, flood-lighted buildings and other subjects in which the time of exposure is a consideration, or if the subject is one with extremes of contrast.

For exteriors, architecture, etc., orthochromatic or panchromatic materials of medium speed, brilliant gradation and a reasonably fine grain are preferred.

Sensitive materials producing still greater contrast are generally preferred for still-life including packaged goods, furniture, decorated china, tapestries, machine parts and general catalog work. The sensitometric characteristics of a typical "commercial" panchromatic film are shown in Fig. 291.

Since extremes of contrast and bright reflecting surfaces are met with frequently in commercial photography, films or plates which have been backed to reduce halation are advisable.

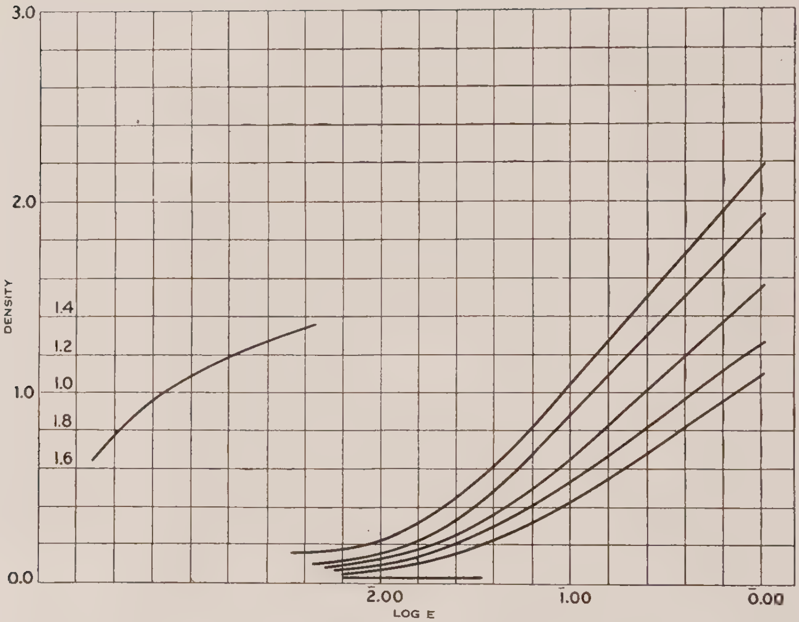


FIG. 291. *D* log *E* and Time-Gamma Curve of a Commercial Panchromatic Material.

Sensitive Materials for Copying.—A medium speed, fine-grain film or plate of brilliant gradation is to be preferred for the copying of photographs and other continuous tone originals in black and white. Ordinary (blue-sensitive) materials are satisfactory with black and white originals unless the paper base is discolored when a color sensitive film or plate and a suitable filter should be employed. Sulfide and other toned prints, or prints which are yellow stained as a result of age, require a panchromatic material and filters.

Films and plates designed for photographing line drawings, printed matter and other "line" or "process" subjects must produce high density and contrast, have high resolution, that is, be able to separate fine lines and have a short exposure range. Sensitometrically, such a material is represented by a characteristic curve having a steep straight line portion with a short foot, or toe, and a high maximum density (Fig. 292). Blue-sensitive materials are suitable for line subjects in black and white but for colored maps, plans in color, blueprints, colored typing, etc., a process panchromatic material must be used.

Sensitive materials of the process type for use in photo-reproduction processes and for micro-copying, will be referred to in a later section, "Specialized Negative Materials."

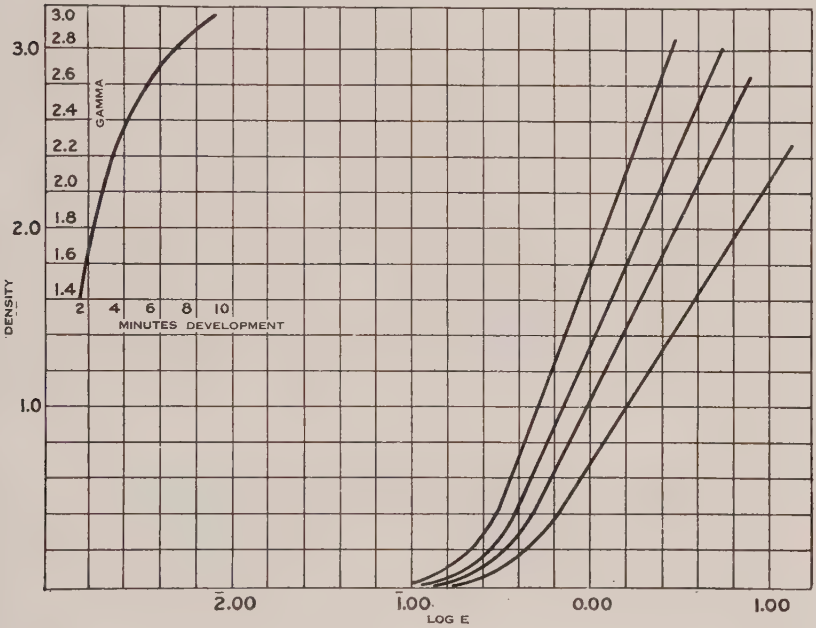


FIG. 292. *D* log *E* and Time-Gamma Curve of a Representative Process Material.

Sensitive Materials for the Miniature Camera.—The growth in the popularity of the miniature camera in the past decade has been due quite as much to the development of emulsions especially suited to its requirements as to the appeal of the camera itself. Modern fine-grain emulsions have in reality made the miniature camera practical, for without them, users of such cameras would be restricted to comparatively small pictures.

The fact that the miniature camera negative must be greatly enlarged and that the resulting print must compare favorably with a contact print of the same size, makes it imperative that the emulsion be capable of recording the detail of the image produced by the lens. To meet this stringent requirement, an emulsion must have exceptional image sharp-

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HIGSON—The Emulsion for a Process Plate. Phot. J. **59** (1919) 266.

ness, high resolving power and fine grain. So much attention has been given to the latter requirement, that the other two are in danger of being overlooked, but the ability of the emulsion to sharply define fine detail—which depends principally on these two factors—is obviously no less important in a film for miniature camera work than the graininess of the image.

A thin emulsion coating has a favorable influence on image sharpness, and resolving power as well as on graininess (see p. 380), but is inferior to a more thickly coated emulsion in exposure latitude, and density range. Some fine-grain materials, chiefly of foreign origin, owe their high image sharpness and fineness of grain, in a large measure, to the use of a thinly coated emulsion. The user of such products must not expect the same exposure latitude and photographic quality available in more thickly coated emulsions.

The sensitometric characteristics of a typical fine grain material of domestic origin are shown in Fig. 293. The exposure latitude, density range and speed of this emulsion compare favorably with other negative materials.

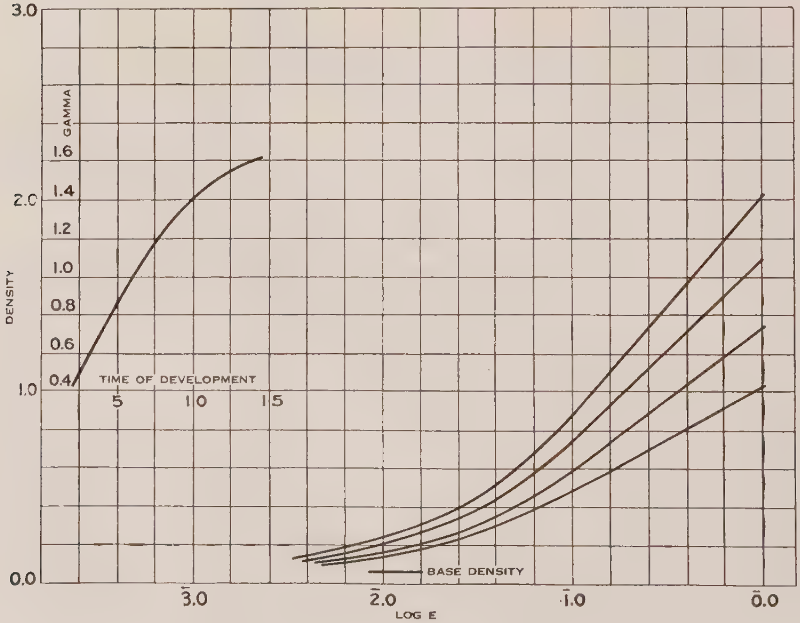

FIG. 293. *D* log *E* and Time-Gamma Curve of a Representative Fine-Grain Material.

Infra-Red Sensitive Materials.—The sensitivity of the eye ends at a wave length of approximately 700 $m\mu$. Recent advances in the dye sensitizing of photographic materials has made it possible to photograph, with comparative ease, the invisible infra-red region as far as 1300 $m\mu$.[16] Most of these infra-red materials are of interest only to the scientific worker; however, materials of the type represented by the spectrograms in Fig. 294 are of general use as they have sufficient speed to permit of instantaneous exposures on out-of-door subjects in good light. An orange or red filter is required to absorb the blue light to which these materials are also sensitive.

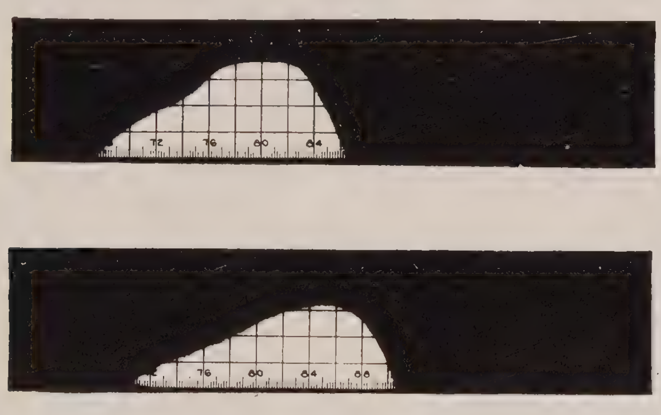

FIG. 294. Wedge Spectrograms of Representative Infra Red Materials.

Infra-red photography is employed in photographing distant landscapes to reveal detail ordinarily lost in atmospheric haze, to produce striking effects in the reproduction of sky and foliage in landscape work, and in medical, documentary and other scientific fields of photography, and in photomicrography.

Recording Papers.—Photocopying papers for use in the *Photostat, Rectigraph,* and similar machines are usually supplied in rolls. Emulsions similar to those used for process materials are employed, but the emulsion coating is much thinner since the image is not used for printing but only for examination by reflected light. Orthochromatic

[16] *Photographic Plates for Use in Astronomy and Spectroscopy,* Eastman Kodak Co.

CLARK—Infra-Red Photography.
SCHWARTZ—Infra-Red Photography. Photo. Tech. I (1940) Feb. p. 8.

emulsions are available for copying originals in color, but no panchromatic photocopying paper appears to be available commercially.

Direct Positive Materials.—It is well known that great over-exposure of a negative emulsion will produce a reversed image, i.e., a negative from a negative or a positive from a positive. With ordinary negative materials, however, the reversed image obtained through over-exposure is so poor in quality as to be of no practical value. Reversal is facilitated and the quality of the reversed image improved if fog-producing agents, such as sodium arsenite, permanganates, persulfates or dichromates, are incoporated in the emulsion and use has been made of this property to produce films which produce a direct non-reversed-copy; i.e., a positive directly from a positive, or a negative from a negative.[17] The speed of these films is approximately that of rapid printing paper. While they are rather slow for general use in the

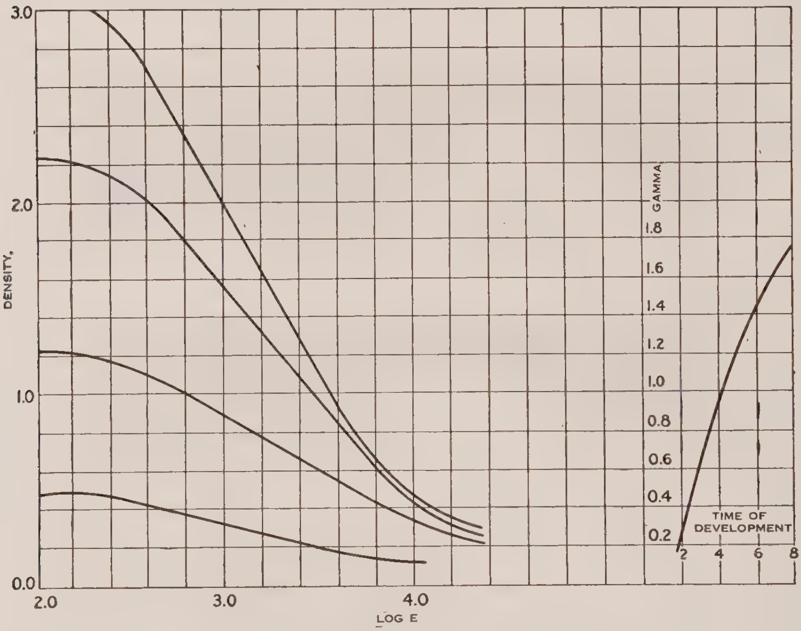

FIG. 295. *D* log *E* and Time-Gamma Curves of a Direct Positive Material (Direct Reversal).

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[17] Arens and Eggert, *Agfa Veroeffentl.* **3** (1934) 166. Barth, *J. Soc. Mot. Pict. Eng.* **27** (1936) 419. Arens, U.S.P. 2,005,837 of 1935. B.P. 443,245.

camera, they are well adapted to making duplicate negatives by contact or projection, making duplicate transparencies and other cases in which a direct copy is required.

Sensitive Materials for Spectroscopy and Astronomy.—Emulsions for photography of the spectrum require high resolving power and image sharpness, fine-grain and sensitivity for that portion of the spectrum under investigation as great as is consistant with the other requirements. For work in the ultra-violet at wave lengths greater than 300 mμ ordinary blue-sensitive materials are satisfactory. Beyond this point, it is necessary to overcome the absorption of ultra-violet radiation by gelatin. While emulsions containing only a trace of gelatin have been used,[18] the usual practice today is to coat a blue-sensitive plate with fluorescent materials, such as mineral oils, which transform ultra-violet radiation into long wave radiation, which is capable of penetrating the gelatin layer and producing a developable image.[19]

Infra-red materials (p. 497) are now available which extend the range of the photographic process to a wave length of approximately 1300 mμ without difficulty.

For astronomical photography, other than spectroscopy, an emulsion of relatively fine grain, good resolving power and high speed at low intensity levels is required.[20] The general practice today is to use high-speed, blue-sensitive or orthochromatic material. For some purposes, as in photographing the solar eclipse during a total eclipse, double-coated plates are preferred because of their greater exposure range.

Plates are invariably used for spectroscopy and astrophotography since the dimensional changes occurring during the processing and drying of film base and upon storage make it undesirable where accurate positional measurements must be made.

Sensitive Materials for Photo-Reproduction Processes.—Special process films and plates have been introduced in recent years for use in photoengraving, lithography and offset, and are rapidly replacing the old wet-collodion process. These new emulsions are thinly coated and have a large amount of silver halide per volume of gelatin. This results in extremely high contrast, high resolving power and image

[18] Schumann plates—See Baly, *Spectroscopy* **II** (1927) 380.

[19] Harrison, *J. Opt. Soc. of Amer.* 11 (1925) 113.

[20] This is a consequence of the failure of the reciprocity law.

Emulsions for Direct Positives. Kodak, Ltd. (Eastman Kodak Co.). B.P. 530,562, June 27, 1939; addition to B.P. 524,087.

sharpness, fine grain and a high density. The sensitometric characteristics of a typical film of this type are shown in Fig. 296.

Emulsions of this type are hardened in manufacture so as to be largely resistant to abrasion or to frilling or scratching in handling. They develop and fix quickly and drying requires only a few minutes. These emulsions are coated on film base of ordinary thickness, on a thin base film which may be printed from either side so as to render stripping and transposition of the image unnecessary, or on paper with a soluble layer between the paper stock and the emulsion, so that the image, after development, may be stripped from its paper support and transferred to glass (stripping paper).

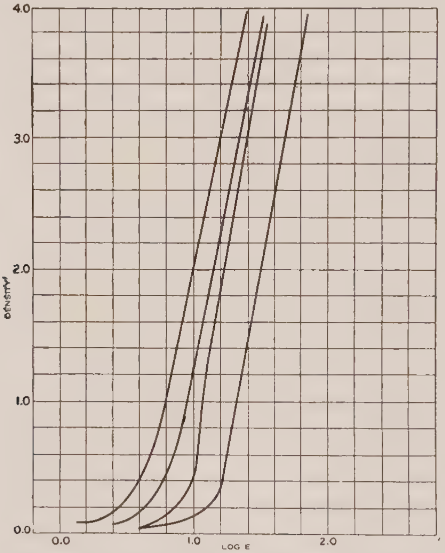

Fig. 296. *D* log *E* Curves of a Representative High Contrast Material for Photomechanical Reproduction Process Work.

Orthochromatic materials of this type are available for use with colored copy.

Sensitive Materials for Aerial Photography.—Sensitive materials for aerial photography should possess high resolving power and produce fine grain images with a relatively high contrast. Orthochromatic film may be used with yellow filters for subjects light in color and in a clear atmosphere, where haze-cutting filters are not required. Panchromatic materials, either of the high speed or fine-grain type, used with yellow or red filters are generally preferred, however, because of the greater latitude in the use of filters. Infra-red sensitive materials are employed for extreme haze penetration in conjunction with deep red filters. For mapping purposes, the emulsion is coated on a special "topographic" support which is specially prepared to have the minimum shrinkage in processing.

Sensitive Materials for X-Ray Photography.—Emulsions for x-ray photography must have high sensitivity to *x-ray radiation* and produce comparatively high density and contrast. With x-ray radiation, the effective sensitivity of an emulsion increases to some extent with the thickness of the coating; hence, sensitive materials for x-ray photography are heavily coated with an emulsion rich in silver halide —up to 50% silver bromide in some cases. Since there is a limit to the thickness of the coating which can be employed without unduly affecting development, or increasing the tendency of the layer to frill in processing, the base is often coated with emulsion on both sides.

Storage of Sensitized Products.—Exposed or unexposed negative material should be kept in a cool dry place where it will be protected from the gases and fumes of such substances, as formaldehyde, hydrogen sulfide, paints, lacquers and paint and lacquer thinners, turpentine in any form, mercury and illuminating gas, all of which tend to produce fog.

Fog may be produced by rewrapping film in paper not designed for that purpose. Either exposed or unexposed material should be wrapped only in the original wrapping papers which have been made especially for this purpose and are free from fog-producing substances.

Exposed plates, or film, which must be kept for some time prior to development in a humid, tropical atmosphere should, if possible, be first desiccated by placing in an air-tight compartment containing calcium chloride, which extracts moisture from the air. After several hours in such a desiccator, the film or plates should be transferred to airtight metal containers and sealed. If this procedure is impractical, the package may be packed tightly in a box filled with crumpled photographic paper which should be removed and dried daily in an oven, or before a fire. Thus protected from moisture, the film will keep in good condition for several weeks, although it is best to arrange for development as soon as possible.

Plates, or film, which are to be transported to hot and humid climates, should be ordered in sealed metal containers. Practically all manufacturers are in a position to supply their negative materials in a special packing for tropical use at a nominal expense.

The storage of reasonable quantities of *safety* base film involves no particular fire hazard. Large quantities should be stored in steel filing cabinets of a type approved by the National Board of Fire Underwriters.[21] Nitrate film in the form of roll film and film pack is excepted, but all other nitrate film should be stored in conformity with the regulations of the Board of Fire Underwriters.

The nitrate base tends to decompose rapidly if stored at temperatures appreciably above normal and, while experience with acetate base is more limited, there is reason to believe that it is chemically more stable than the nitrate base. However, unless stored at a relative humidity of about 50% or higher, acetate base loses its flexibility, and becomes brittle. This ordinarily is of no real consequence except in the case of motion picture film. The flexibility of negatives or positives on an acetate base film which have been stored in a warm, dry atmosphere, may be partially restored by rehumidifying. Studies of the stability of film base at the United States Bureau of Standards, indicate that acetate base film is as durable as the best rag paper stock if stored under the proper conditions.[22]

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[21] Regulations for the storage and handling of photographic and x-ray films. Natl. Board of Fire Underwriters, 85 John St., New York City.

[22] Scribner, *Natl. Bur. Stand. Miscl. Publ.* M 162, Government Printing Office, Washington 1939. Hill and Weber, *J. Bur. Stand.* **17** (1936) 871; *J. Soc. Mot. Pict. Eng.* **27** (1936) 677.

CHAPTER XVII

EXPOSURE OF THE NEGATIVE

Theory of Exposure.—Photographic exposure is defined as the product of time and intensity of illumination acting upon the photographic material. A series of exposures may be produced, therefore, by a variation in either the time of exposure or the intensity of the illumination. When a photographic material is exposed in the camera, the time factor is constant and the variation in exposure for different parts of the image is directly proportional to the brightnesses of the corresponding parts of the subject, except for differences produced in the image-forming system.

Usually, the essential requirement is that the photographic record of these brightnesses create the visual impression of the original subject. It is, however, only within a certain exposure range that a sensitive material is able to record differences in brightnesses correctly. Strictly speaking, this range in exposure is indicated by the straight-line portion of the $D \log E$ curve of that particular film or plate. In practice, however, portions of the curve at both extremities of the straight-line portion may be used without producing evident falsification of brightness values.

The problem in exposure, therefore, is to adjust the time factor so that the exposures produced by the various brightnesses of the subject are within the exposure range which produces a satisfactory reproduction of the subject on the plate or film employed.

It should be noted at this point that, with practically all negative materials, the available exposure range is several times greater than the brightness range of the subject, so that there is, practically speaking, no one correct exposure but a *period* of correct exposure, i.e., a range of exposures any one of which will produce negatives from which satisfactory or, within certain limits, *identical* prints may be made.

Factors Determining the Time of Exposure.—Fig. 297 illustrates the principal factors involved in the determination of the time of exposure.[1] The six principal factors are: (1) illumination, (2) subject,

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[1] Adapted from "Photographic Speed Ratings" by Fowler and Varden, *American Annual of Photography*, 1940, p. 169.

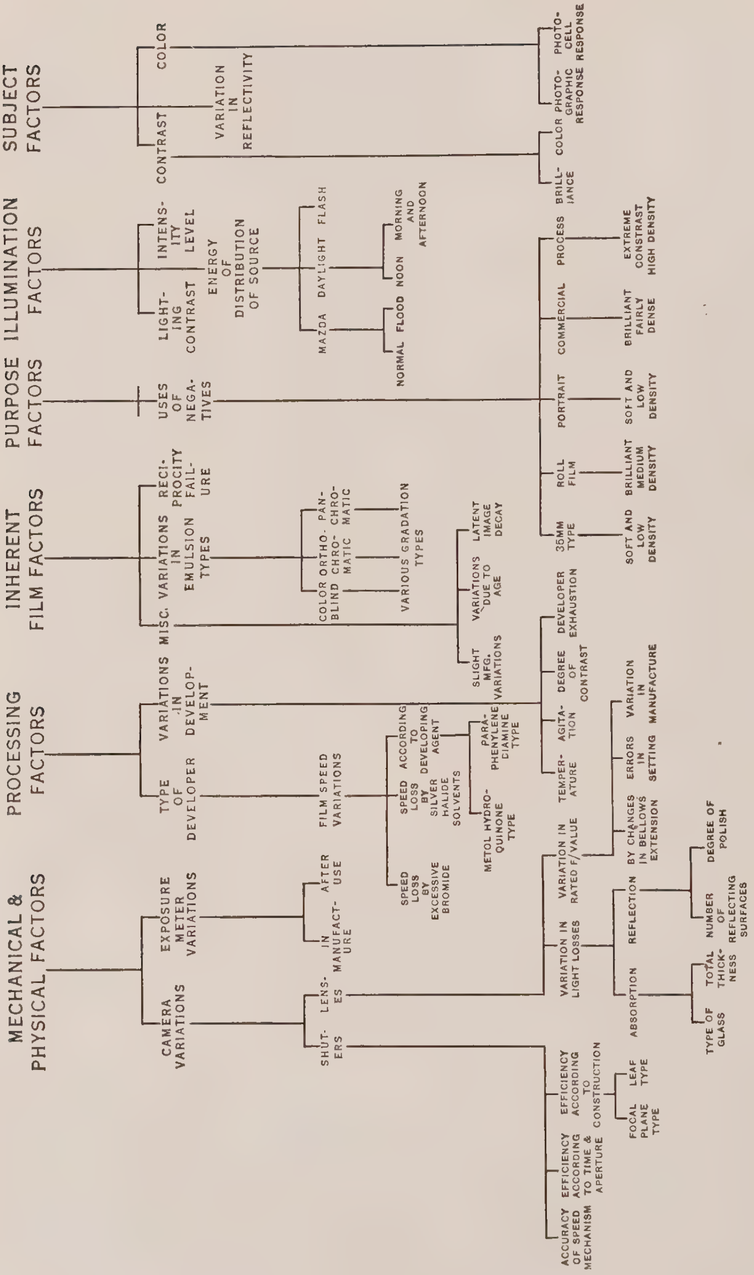

Fig. 297. Factors Involved in the Exposure of the Negative.

(3) sensitive material, (4) processing, (5) purpose and (6) mechanical and physical factors.

Illumination. Both the intensity and the color characteristics of the illumination on the subject are important factors in exposure.

In the case of sunlight, the intensity of illumination is determined by the time of year, the time of day and by atmospheric conditions.

The intensity of unobscured noon sunlight varies from month to month with the latitude being at a maximum in the northern hemisphere in June and at a minimum in December. The principal variation in the intensity of sunlight from month to month, however, is in the length of the day. The variation of unobscured sunlight from hour to hour is comparatively small in the middle of the day, but changes rapidly in the early morning hours or the late afternoon.

The intensity of sunlight is, of course, materially affected by clouds, smoke, dust and other atmospheric disturbances. A slight haze resulting in shadows which are barely visible, requires from two to three times the exposure of unobscured sunlight. A clouded sky, with the sun itself barely visible, requires an increase in exposure of from four to five times. Heavily over-clouded skies require an increase of from six to sixteen times in exposure, differences in illumination under such conditions being extremely difficult to estimate visually or to describe.

With artificial light sources, the illumination on the subject depends upon the intensity of the source and the distance. Reflectors may increase the effective illumination many times.

Another important factor in exposure is the color of the light. The response of any photographic sensitive material varies greatly with the wave length of the incident radiation (p. 457). A blue-sensitive material, for example, has practically all of its sensitivity in the ultraviolet, violet and blue portions of the spectrum. It can, therefore, utilize a much larger portion of the light from a source of daylight quality than from tungsten illumination. See Fig. 271 and Fig. 272. The difference is less marked but still exists with orthochromatic and panchromatic material.

The color temperature of sunlight is greatly affected by clouds and dust. Clouds, by reducing the amount of direct sunlight, may increase the effective color temperature (p. 168). At other times, as when the sun is near the horizon, the color temperature is reduced, i.e., the light becomes yellowish. Panchromatic materials, therefore, require relatively less exposure in the early morning, or late afternoon, hours than blue-sensitive or orthochromatic materials.

The response of the eye is quite different from that of photographic materials; consequently variations in the color of the light which result in substantial differences in exposure are not readily discernable to the eye.

While with long experience, the eye may acquire the ability to distinguish differences in illumination under conditions with which it is familiar, in general the eye is a poor judge of the intensity of illumination, unless aided, nor is it able to evaluate the variations in color which affect exposure. Hence, such classifications as intense light, bright light, light clouds, dull, etc., while helpful, are only approximations.

The subject. Since the subject is not always fully exposed to the direct light of the sun or the sky, its location may have an important bearing on the illumination which it receives. In a narrow street, for example, the illumination is greatly reduced by the buildings on either side which permit light from only a small strip of the sky to reach the subject. Likewise, in heavily wooded areas or in shaded places, under porches and the like, the illumination is greatly reduced. It is extremely difficult to estimate the illumination visually under such conditions and, while it is possible to make some allowance for the subject factor by classifying the more common subjects into groups, more errors in exposure probably result from the difficulties arising from this source than from any other.

Moreover, subjects differ greatly in the proportion of the light falling on them which is reflected. A subject containing only water and sky, for example, reflects a larger proportion of the light falling on it than does a distant landscape, and this in turn more than a landscape in which are figures, trees, shrubbery, buildings or other dark colored objects near the camera. In general, the nearer the subject is to the camera, the larger the shadow areas and the less the amount of reflected light.

In evaluating the amount of light reflected, or the brightness, the quality of the light, or its color, must be considered with particular reference to the color sensitivity characteristics of the photographic material. The more nearly the color response of the film or plate approaches that of the eye, the less the difficulty experienced in evaluating the allowance to be made for the color, or colors, of the subject.

The brightness of the optical image. The difference in the brightnesses of the optical image on the film, or plate, and those of the subject itself is proportional, within certain limits, to the f/number of the lens. It should be noted, however, that the brightness of the optical image varies with the distance from the axis. Consequently, the exposure required for an object on the axis is less than that for an object of equal brightness near the margins of the field. This difference may be as great as 1 : 3 in the case of wide angle lenses. Ordinarily, little attention is given to the loss of light by reflection and absorption in the objective. That these losses may be considerable is evident from the following table [2] which shows the marked f/number, the actual percentage transmission and the effective f/number of several different types of photographic objectives:

Objective	*f/Number*	*Transmission*	*Effective f/No.*
Ernostar	$f/2$	46.6%	$f/3.1$
Kinoplasmat	$f/1.5$	38.7%	$f/2.82$
Tessar	$f/4.5$	63.5%	$f/5.94$
Aviar	$f/4.5$	49.7%	$f/6.65$
Collinear	$f/6.3$	53.4%	$f/8.67$

Speed of the sensitive material. There are five methods of expressing the speed of a sensitive material in more or less general use in the United States: (1) Weston speeds, (2) General Electric speeds, (3) Kodak speeds, (4) Scheiner numbers and (5) DIN numbers.

The Weston and General Electric speeds of negative materials are determined periodically by the Weston Electrical Instrument Company and the General Electric Co., respectively, and published primarily for use with their own meters. A number of other meters, however, are licensed to use Weston speeds.

Kodak speeds are determined by the minimum useful gradient and, at present, are available only for negative materials of the Eastman Kodak Company.

Scheiner numbers are not officially recognized by any manufacturer of negative materials in the United States. There are, however, a number of exposure meters marked in so-called Scheiner numbers. These numbers are not true Scheiner numbers as they are not determined from sensitometric measurements in the laboratory in accordance with Scheiner's method, but from comparative exposure tests.

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[2] Forch and Lehrmann, *Kinotechnik* (1928) **103**.

DIN numbers likewise are not officially recognized in the United States and are met with only on sensitive materials and exposure meters imported from Germany or German-speaking countries.

Of the various speed rating systems which have been devised, that based upon the limiting useful gradient would appear to be the one most in accord with photographic practice, since it is the only one in which the requirements of the printing medium receive consideration and a negative is satisfactory only if it produces a satisfactory print.

The various systems of speed rating are based upon different experimental procedures and employ different criteria in determining speed; hence, an exact comparison is impossible and two films having the same speed rating in one system may have quite different speed values in all other systems.

The following table indicates approximately equivalent speeds in the different systems. Exposures based upon these values should be within the useful exposure range of good negative materials.

COMPARISON OF SPEED RATING SYSTEMS

Weston	*Kodak Minimum Gradient*	*Amer. Scheiner*	*Europe. Scheiner*	*Europe. DIN*	*H. & D. (British)*	*H. & D. Used on Europe. Cont.*	*Relative Exposure*
6	30	17	23	13/10	400	1300	4
8	40	18	24	14/10	500	1700	3⅓
10	50	19	25	15/10	600	2100	2⅔
12	60	20	26	16/10	750	2700	2
16	80	21	27	17/10	1000	3500	1⅔
20	100	22	28	18/10	1200	4400	1⅓
24	140	23	29	19/10	1500	5600	1
32	170	24	30	20/10	2000	7200	⅘
40	200	25	31	21/10	2500	9100	⅔
50	250	26	32	22/10	3000	11600	½
64	320	27	33	23/10	—	—	⅖
80	400	28	34	24/10	—	—	⅓
100	500	29	35	25/10	—	—	¼
125	625	30	36	26/10	—	—	⅕

If the speed of a sensitive material is defined as the reciprocal of the exposure necessary for a satisfactory negative, the only comprehensive and adequate definition from the standpoint of practical photography, then there is no one number which will properly represent the speed of a given film or plate, except under certain specified conditions, for the practical speed depends upon the way in which the material is used and the result required. A number of the more important of these conditions are enumerated in the chart at the beginning of this chapter.

Processing conditions may have an important bearing on the effective speed of a film or plate. Excepting certain low potential developing agents used chiefly in fine grain developers, variations in speed due to the use of different developing agents are generally of minor importance. This is not true, however, of the degree of development (gamma) or the degree of exhaustion of the developing solution. In general, the effective speed increases with the degree of development and the increase is considerable with some modern emulsions. Losses in effective speed, due to the use of partially exhausted developers, are frequently considerable and often are not recognized because the contrast and density of the highlights has not been affected to the same degree as that of the shadows.

Exposure Meters.—There are essentially two types of exposure meters: (1) those which measure the intensity of the light on the subject by the rate of darkening of a sensitive paper, and (2) those in which the light reflected from the subject is measured by visual methods or by means of a photo-electric cell. Meters of the first type (actinometers) were the first to find general acceptance; they have been replaced almost completely in recent years, however, with instruments of the second class and in particular those employing photo-electric cells.

Actinometers.—Among exposure meters of this type, the best known, in English speaking countries at any rate, are the Watkins and the Wynne. The Watkins is no longer made, but the Wynne is still available. Both utilize the darkening of sensitive paper to a standard tint which, however, differs in the two meters. The meter is held to face the light illuminating the darkest part of the subject and the time for darkening of the paper to the standard tint is determined. This time, the actinometer time as it is called, is an indication of the intensity of the light and from it the exposure required with a given lens aperture and plate or film is calculated with the aid of the movable scales which form a part of the instrument. In the case of the Watkins meter, the first visible darkening of the sensitive paper requires 1/16 of the time necessary for the standard tint; hence indoors, or where the light is poor, the time required for making a test of the light may be reduced by using the sixteenth tint as it is called.

The weak point of the actinometer is that it can measure only the light falling on the subject and not that reflected from it. However, if the proper allowance is made for different subjects, the exposure indications of an actinometer produce a high percentage of satisfactory results.

Visual Exposure Meters.—Exposure meters of this type may be divided into two classes: (1) those in which the illumination reflected from the subject is measured by the disappearance of detail in the shadows, or an artificial test object lighted by the subject; (2) those in which the illumination is measured by comparing it with the light of a small electric lamp operated from flashlight batteries.

Instruments of the first class may be further divided into two subclasses: (1) those in which the subject is viewed through an optical wedge, which for convenience is usually circular, and this is revolved past the eye until detail in the shadows disappear, or are barely visible. the proper exposure is then determined from the scales of the instrument at this setting. (2) In the second are meters in which the light reflected from the subject illuminates an artificial test object, usually a transparent figure, the visibility of which may be reduced in a measurable manner by means of an optical wedge or an adjustable diaphragm. In some examples, a number of figures varying in visibility are seen when the meter is pointed at the subject and the number just barely discernible is taken as a measure of the light reflected from the subject. The advantage of meters of this type over those described in class one is in the certainty with which the extinction point can be determined. On the other hand, when used at the camera, the average brightness of the subject is measured and not that of any particular part. The total brightness of the subject may, or may not, be a satisfactory indication of the proper exposure. If, for example, a large portion of the subject is brightly illuminated and the shadow area is small, an exposure based upon the total amount of light reflected by the subject may result in underexposure of the shadow areas. All meters which measure the total amount of light are open to this objection which, however, may be overcome to some extent if the shadow area can be approached so as to exclude the remainder of the subject in making the measurement.

In all visual type meters, it is the visual brightness of the subject which is measured and not the actinic brightness, which may be quite

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Smethurst—Reflected Light as a Criterion of Exposure. Brit. J. Phot. **85** (1938) 533, 548, 566.

Gundelfinger and Stafford—Photometric Determination of Camera Exposures for Motion-Picture Work. J. Franklin Inst. **215** (1933) 81.

different. The eye and photographic materials differ considerably in their response to different colors, therefore, the visual brightness is not an accurate indication of the exposure required in the case of an object involving color. In most meters, this difficulty is partially overcome by the insertion of a blue-violet screen in the field of vision. Visual measurements of brightness then correspond more nearly with the actinic brightness, but this expedient naturally fails to take into consideration the differences in photographic materials with respect to color sensitivity.

The accuracy of meters in which brightness is measured by the extinction of detail in the subject, or an artificial test object, are affected by the ability of the eye to adjust itself to variations in the intensity of illumination over a fairly wide range. Thus on coming into a darkened room, the eye soon adjusts itself to the weaker illumination and we shortly begin to see detail that was totally invisible when we entered the room. Consequently, the exposures indicated by the meter will not accurately represent the real difference in the intensity of the illumination on the two subjects. The result is that another correction factor has to be applied to the meter readings of interior work.

Two examples of exposure meters in class 2 are now on the market. In both the light reflected from the subject is measured by comparison with that from a small electric lamp operated from flashlight batteries, the intensity of the light from the lamp being controlled by means of a variable resistance.

In one of these, the light reflected from the subject illuminates one-half of the photometric field, the other half of which is illuminated by the comparison light. In the other example now on the market, the image of a cross formed by the comparison light is superimposed on the image of the subject in a finder. The illumination of the image of the cross is varied, by means of a knob operating a variable resistance, until it equals that of the particular brightness of the subject being measured. The exposure is then determined from a scale calculator which is operated by the knob, controlling the variable resistance. This design has the advantage that the brightness of any part of the subject may be measured.

Meters of this type have been made to measure the brightness of the image or the focusing screen but have never found general acceptance.

Photocell Meters.—In recent years, exposure meters employing light sensitive photocells have come into general use. While not a complete solution of the exposure problem, such instruments affording as they do a convenient and accurate means of measuring illumination are of very real assistance in determining exposures.

With one exception, meters of this type employ a photovoltaic, or "self generating" cell. The photovoltaic cell consists of a layer of light sensitive material which is usually copper oxide formed on a copper disk and covered with a transparent layer of gold.[3] When this cell is exposed to light, radiant energy is converted into electrical energy. The electrical current produced by connecting the two terminals can be measured by means of a microammeter, and is almost directly proportional to the intensity of the illumination on the cell. The photovoltaic cell thus provides a self-contained, portable and highly accurate means of measuring illumination, thus readily adapting it to the requirements of an exposure meter. As there is no physical or chemical change in the cell itself, its life is supposed to be practically unlimited. The color sensitivity of the cell is similar to that of the eye (Fig. 298) but extends further into both the red and the ultra-violet. The response of the cell to violet and blue is relatively greater than that of the eye, but not so great as that of photographic materials. It is possible, of course, by means of suitable filters to make the response of the cell identical with that of the eye or a given photographic material, but the difference is not of sufficient importance in the determination of photographic exposures to justify the added expense.

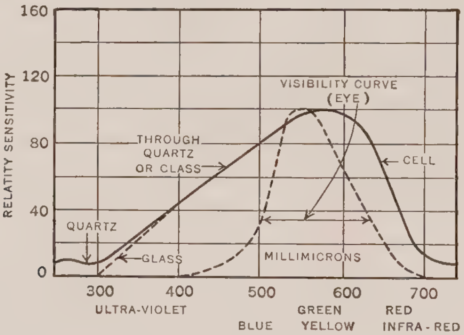

Fig. 298. Curve of the Spectral Response of a Typical Photocell Used in an Exposure Meter.

The disadvantage of the photovoltaic cell is its low voltage output and as this cannot be easily increased by amplification, the sensitivity of the cell is such that it can be used only to measure the light reflected from relatively large areas of the subject, and difficulty is experienced frequently in making measurements in interiors and other poorly lighted subjects.

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[3] In some cases, copper is replaced with iron and the copperoxide with selenium.

The exception referred to in the preceding paragraph is an instrument employing a phototube. The phototube differs from the photovoltaic cell in that it does not generate an electric current, but functions as an electrical conductor only when exposed to light. It consists of an anode and a cathode in a gas filled or vacuum tube. When exposed to light, electrons are emitted by the cathode and if an electric current of the proper voltage is applied, the electrons travel towards the anode conducting an electrical current. This current is almost directly proportional to the illumination on the cathode over a comparatively wide range. Thus, it is possible to measure illumination directly without reference to the eye from the electrical output of the cell as indicated on a suitable galvanometer. Tubes of this type are more sensitive than the photovoltaic cell, as the output is easily amplified with suitable amplifying equipment. The sensitivity is such as to make possible the measurement of small areas (about 1/32 inch) of the image on the focusing screen of the camera, or the enlarging easel. On the other hand, this type of light measuring instrument has the following disadvantages:

1. It is more delicate and requires more careful and skillful handling.
2. It is larger and more expensive.
3. It must be connected with a 110 volt electrical circuit, or in some cases, with batteries, which limit its use except in the studio or where electric current of the proper type is readily available.

Use of Photocell Exposure Meters.—In most cases, it is sufficient to measure the total, or integrated, brightness of the entire scene from a point near the camera or preferably from a point at which only that part of the subject which will be included in the picture is within the light-acceptance angle of the meter. When the exposure is determined in this manner, however, the highlights very largely determine the reading obtained since they reflect more light than the shadows. Thus, if the subject is one which is generally well lighted, but contains dark objects near the camera, an exposure based upon the integrated brightness may lead to underexposure of the darker portions. Out-of-doors, care should be taken not to include too much of the sky or the brightness measurement may lead to underexposure.

On the other hand, with a subject which is generally dark but contains a well lighted area, the latter may be overexposed. With such subjects, it is best to measure the brightness of that portion of the subject which is the most important. This may be done by making the measurement from a position which is sufficiently close to include only the light reflected from the area in question. The angle included by the cell varies in different meters but generally if the distance from which the measurement is made is approximately equal to the shortest dimension of the area, whose brightness is to be measured, the results will be sufficiently accurate for practical purposes.

The lowest brightness which can be accurately measured varies slightly with different meters, but is usually on the order of 1/10 foot-candle. The brightness of objects too dark to be measured directly may often be determined as follows: First measure a portion of the object having the same general tone on which the illumination is sufficient for a measurement to be made. Then measure the brightness of a sheet of white paper placed in the same position. The ratio of the two brightnesses gives the reflection coefficient of the paper. Then, place the paper in the darker area and measure the light reflected by the paper. Divide the value thus obtained by the reflection coefficient of the paper and use the brightness value thus obtained in calculating the exposure.

In determining the exposure for films or plates for reversal processing, many authorities are in favor of measuring the greatest brightness of the subject in which detail is desired, so as to be able to obtain consistently, upon reversal, a positive image in which the maximum highlight is represented by the lowest density with which satisfactory reproduction can be obtained. Others have recommended the use of an artificial highlight of white or gray cardboard.

Exposure Required to Stop Motion.—The amount of displacement possible in the image of a moving object without producing visible unsharpness depends upon the allowable circle of confusion (p. 71). In general, it is customary to regard as allowable a circle of confusion equal to 1/1200 of the focal length of the lens. If, however, the image is to be greatly enlarged, a still smaller circle of confusion is necessary.

SMETHURST—The Gauging of Exposures by Meter and Standard Subjects. Brit. J. Phot. **85** (1938) 212.

SMETHURST—Reflected Light as a Criterion of Exposure. Brit. J. Phot. **85** (1938) 533, 566.

WEST—Meters for Color Exposures. Phot. J. **79** (1939) 577.

COBB AND LOWE—The Neutrome Gray Exposure Aid. Phot. Tech. **2** (1940) Sept. p. 19.

The amount of the displacement of the image of a moving object in a given time interval depends upon four factors:

1. *The velocity of the object.* The displacement of the image is obviously proportional, other factors being constant, to the velocity of the moving object. Usually this is unknown but in certain cases it may be estimated with sufficient accuracy for practical purposes. One knows, for example, within certain limits what speed to expect of runners at the finish of any of the usual distances, of horses coming down the home stretch, and in many other athletic and sporting events. It must be remembered that allowance must be made for the more rapid movement of the arms and legs which move approximately twice as fast as the body itself.

2. *Distance of object from camera.* The nearer the moving object is to the camera, the larger the image and the greater the displacement for a given exposure. Except for very short distances, the displacement of the image for a given exposure is inversely proportional to the distance of the object.

3. *The focal length of the lens.* For a given object distance the longer the focal length of the lens the larger the image and the greater

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Berg—Mechanism of the Photographic Process. Phot. J. **78** (1938) 286.
Benford—Exposure Chart for Filters. Phot.Tech. **2** (1940) Sept. p. 63.
Goodwin—The Photronic Exposure Meter. J. Soc. Mot. Pict. Eng. **20** (1933) 95.
Harrison—Photoelectric Exposure Meters. Phot. J. **79** (1939) 389.
Harrison—Photoelectric Exposure Meters. Phot. J. **74** (1934) 169.
Keinath—Photoelectric Exposure Meters. Phot.Tech. **3** (1941) Jan. p. 56.
Macadie—Basic Points in the Design of Photoelectric Exposure Meters. Brit. J. Phot. **85** (1938) 771.
Michaelson—Integrating Exposure Meter. Phot. Tech. **2** (1940) Feb. p. 43.
Milbauer—Tests of Exposure Meters. Brit. J. Phot. **84** (1937) 837.
Moen—A Precision Instrument for the Determination of Exposure. J. Brit. Kine. Soc. **1** (1938) 99.
Norwood—Studies of Photoelectric Exposure Metering. Amer. Cinemat. **20** (1939) 499; **21** (1940) 18, 44, 64, 119.
Seager—The Technique of the Exposure Meter. Amer. Annual of Phot. **52** (1938) 12.
Swain—Exposure Table for Photoflood. Phot. Tech. **1** (1939) Oct. p. 23.
Turner—More About Exposure Meters. Brit. J. Phot. **82** (1935) 789 (general).
Williams—Characteristics of Photoelectric Exposure Meters. Phot. Tech. **1** (1939) June p. 37.

the displacement of the image in a given time interval. Thus the displacement of the image, under given conditions, varies directly with the focal length of the lens.

4. *Direction of movement.* With an object moving in a direction at an angle to the optical axis of the lens, the displacement of the image is the sum of the displacement due to the lateral movement of the object and the movement in line with the axis.

The time of exposure permissible in the case of an object moving at right angles to the optical axis of the lens is indicated by the equation

$$E = \frac{D + F}{S \times 100F},$$

where E = Exposure in fractions of a second,
F = Focal length of lens in inches,
D = Distance of object at time of exposure in inches,
S = Speed of objects in inches per second,
100 = Denominator of fraction indicating allowable circle of confusion.

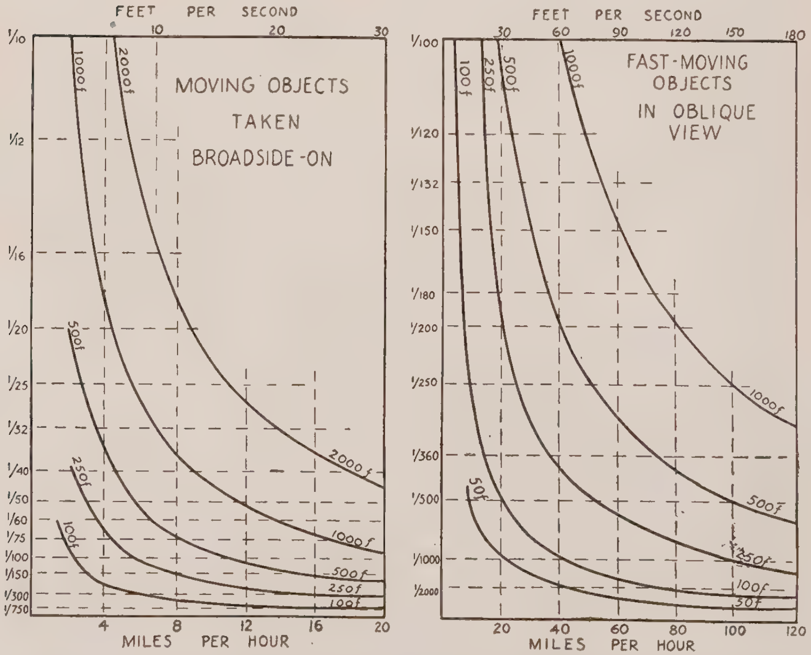

FIG. 299. Curves for the Calculation of the Approximate Time of Exposure Necessary to Stop Motion, the Distance of the Moving Object Being Shown as a Multiple of the Focal Length of the Lens. (*British Journal of Photography.*)

For practical purposes, this may be written

$$E = \frac{D}{S \times 100}.$$

For an object moving directly to or from the camera, the equation is

$$E = \frac{(D + F)^2}{S \times 100F \times (A/2)},$$

in which E, D, S, and F have the same significance as in the previous equation and $(A/2)$ represents the depth of the object in inches.[4]

For an object moving at an angle to the optical axis of the lens, the permissible exposure is given by

$$E = \frac{D + F}{S \times 100F \times \cos\theta} \frac{(D + F)^2}{S \times 100F \times (A/2) \times \sin\theta}.$$

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[4] Cleveland, *Amer. Phot.* (1925) 386, 442. See also Cummings, *Brit. J. Phot.* **70** (1923) 447.

CHAPTER XVIII

NEGATIVE DEVELOPMENT

The Darkroom.—When space is not available for a permanent darkroom, as is often the case in an apartment or in rented quarters, rooms used for other purposes must be made to serve as a workroom. Aside from the fact that it must be a room which can be made perfectly light-tight when required without too much delay, the major considerations are ready access to electricity and running water. At night, almost any room can be made light-tight, if the windows are covered with a dark cloth to exclude the light from nearby street lamps, passing automobiles, etc. If daytime use is contemplated, a shutter of wall board held in place with turn buttons attached to the window frame may be required.

The kitchen is, in many cases, the best choice as it ordinarily provides the necessary electrical outlets together with running water and a sink in which developing and other trays or tanks may be placed. The bathroom usually has fewer windows to be covered and may have the electrical outlets needed. Running water is available, of course, but the lavatory and bathtub are not as well adapted to the requirements of photographic work as the kitchen sink. A shower compartment, however, can be made to serve by installing a work table and has the advantage of providing a floor drain in the event that chemicals or solutions are accidentally spilt.

Closets are frequently available and the ease with which the average closet can be made light-tight is a great temptation, but in all other respects it is not a suitable location. It may have the necessary electrical outlets, but it seldom has running water and the installation of either is expensive and frequently out of the question in rented quarters. In addition, the space is usually limited and no provisions have been, or can be, made for adequate ventilation. In case nothing better is available, a closet may be made to serve for the loading of tanks, film holders and magazines and other operations which necessitate only a brief stay in the darkroom and do not require running water or the usual facilities of a well equipped workroom. In this case, a work shelf should be constructed at a convenient height along one side and covered with oilcloth or painted with a waterproof lacquer, so that it may be wiped dry after use and thus avoid, so far as possible, the accumulation of dampness in the room. If a wooden strip is attached to the outside edges of the shelf and the oilcloth folded over it so as to form a waterproof tray, so much the better.

If one is compelled by circumstances to work in a room used for other purposes, consideration may well be given to the installation of a cabinet, or cupboard, in which developing paraphernalia, such as trays, graduates, timers, etc., as well as solutions and sensitive materials can be kept when not in use and be out of the way, yet readily available when required. If the space is available, attention may be given to the construction of a cabinet which, like a kitchen cupboard, will also provide a work bench for developing and printing. It is not impossible to build into this a small sink and with some additional expense to provide for running water, by permanently connecting with the water lines, or if the cabinet must be movable, by a rubber hose connection to the kitchen sink. Usually in the latter case, the only real difficulty is in providing for a drain. The simplest method is to make the level of the sink in the cupboard higher than that of the kitchen sink so that the water can drain directly from one sink into the other. This often places the work bench inconveniently high in which case it may be necessary to install a separate drain to which a connection can be made. The cabinet should be wired so as to provide the necessary outlets for safelight lamps, electric timers, a printer and an enlarger. The wiring, like the plumbing, should be installed by a competent workman to make certain that it meets the required standards and that the capacity of the house wiring circuit is not exceeded.

If a permanent darkroom is possible, the first problem is its location. Usually the attic or the cellar are the first places considered. The attic is often attractive because of the space available. Running water, however, is not usually available and is not easily installed. In addition, it is usually hot in summer and cold in winter. Both water and electrical outlets are ordinarily available in the cellar or may be installed at lower cost than almost anywhere else. In some cases, dampness may be of some concern, but may be overcome by the installation of a heating unit or by storing sensitive materials which would be affected in another part of the house. The cellar has the advantage that the temperature is generally more uniform throughout the year and that

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Hoag—Build a Portable Darkroom. Popular Phot. **6** (1940) June p. 57.

Parker, Jr.—Darkrooms for Every Budget. Popular Phot. **7** (1940) October p. 20, 111.

overflows from leaking sinks, etc., are less serious than on the upper floors of the building.

The location having been decided upon, the next consideration is that of size. Limitations of space are often the determining factor; in general, however, a space about 5 × 6 feet should be regarded as the minimum. Less than this does not provide sufficient space for an enlarger, which is a necessity in any completely equipped workroom. Moreover, a darkroom smaller than this does not provide sufficient space to separate operations involving the use of solutions from those, such as contact and projection printing, where water from any source is objectionable. In this, as in other matters, the builder-photographer must study carefully both the space available and that needed for the different kinds of work which he hopes to do, and plan accordingly.

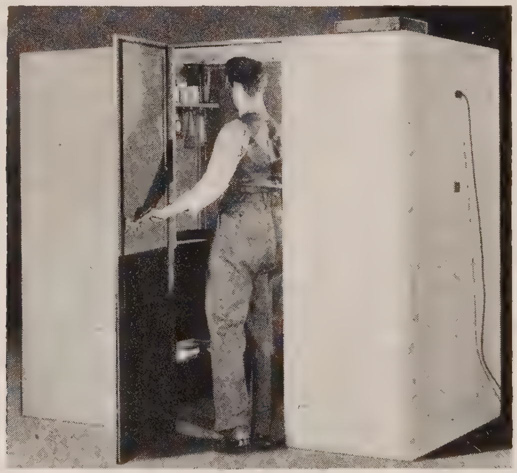

FIG. 300. Ready-built Darkroom (Regent Specialties Co., Rochester, New York).

The wall partitions may be of ordinary frame construction of 2 × 4's plastered, or covered with plasterboard or wall board, preferably in the latter case, of the waterproof type. Particular care must be taken to ensure a light-tight yet free moving door. Most contractors and carpenters have very little idea of the steps necessary to make doors, ventilators, etc., light-tight. A broader door jam than is customary is usually necessary, if a door is to be made reasonably light-tight, and a weather strip is useful as an added precaution.

For those who do not wish to undertake such construction themselves, a ready built darkroom may be purchased (Fig. 300).

Ventilation.—Adequate ventilation should receive consideration when the walls are planned and built. If the wall partitions are constructed of wall board on each side of the 2 × 4's, baffles may be installed between openings in the two walls to admit air and yet prevent the entrance of light. Light-tight metal ventilators of the type shown in Fig. 301 are obtainable from dealers and may be used instead. For small darkrooms, the Eastman Darkroom ventilator (Fig. 302), a small electrically driven centrifugal blower delivering 35 cubic feet of air per minute, is satisfactory. It is mounted in the partition and contains tight traps to cover both the outlet and inlet. Larger units (Fig. 303) up to a capacity of 500 feet a minute are obtainable from the Ilg Electrical Manufacturing Company, Chicago, Illinois.

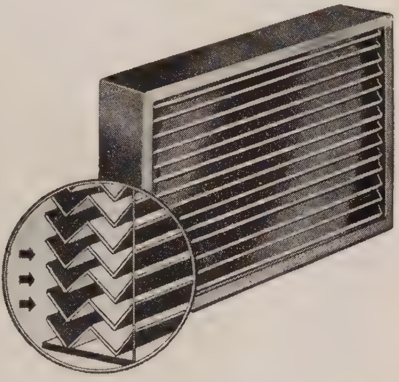

Fig. 301. Metal Ventilator for Installation in Wall of Darkroom.

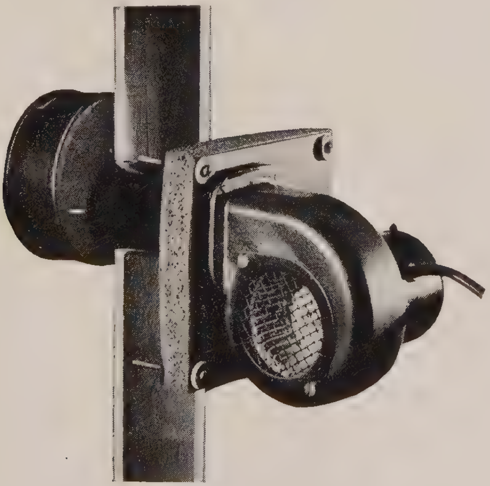

Fig. 302. Eastman Darkroom Ventilator.

Floors.—A waterproof floor with a drain is a desirable feature, particularly if the darkroom is on the upper floor of a building. The installation of a floor drain necessitates the construction of a subfloor from 4 to 6 inches above the regular building floor. Concrete with a waterproof surfacing forms a good floor, but is rather heavy, and where weight is a consideration, a well-laid wooden floor may be covered with hard-rubber tile, blocks, mastic or even linoleum.

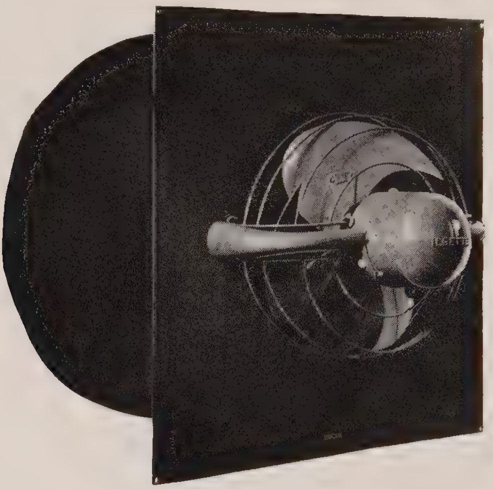

FIG. 303. Ventilating Fan for Larger Darkrooms.

Sinks.—The sink is a very important feature of any darkroom and its placement, size and construction all deserve careful consideration. Placement will be considered later, but so far as size is concerned, the sink should be large enough to take three trays of the largest size which one expects to use and the depth should be sufficient to prevent the splashing of running water, or solutions, over the edge onto the floor. Enameled iron sinks are practically the only type available in the size and depth required, but as these are rather expensive, it may be more economical to build the sink. Alberene stone is one of the best materials, but is expensive and must be carefully installed to prevent cracking. Stainless steel (18–8) is excellent, but expensive. Lead and concrete are rather too heavy and bulky for the average darkroom. A *well-fitted* wood sink coated with Kodacoat paint or nitrocellulose lacquer is reasonably satisfactory if repainted frequently, as is heavy galvanized metal coated with Kodacoat or black asphaltum paint.

Unless the sink is a large one and occupies the side wall of the room to which it is attached, it is well to increase the working space around it by installing drain boards on either side, or a work bench may be constructed across that side of the room and an opening cut in it for the sink. The drain boards, or bench, may be covered with waterproofed masonite and lacquer or with linoleum or rubber sheeting.

If available, both hot and cold water should be installed. A mixer tap is a decided convenience, but should be in addition to separate cold water tap. More than one cold water tap is frequently needed at the same time.

Wiring.—All wiring should conform to the underwriter's specifications and for this reason a competent electrician should be employed. The use of temporary, makeshift electrical wiring cannot be too strongly condemned. Temporary expedients have a way of becoming permanent and the dangers involved are ignored until something happens—and then it is often too late. In planning the wiring of the darkroom, separate outlets should be provided for every piece of electrical equipment and these outlets should be placed as near as possible to the place to be occupied by the equipment so as to keep the connecting cords short. Each outlet should have its own contact switch. It is well to include, in the wiring diagram, several outlets beyond those required at the time to provide for additional lights, timers, fans, heating coils or hot plates and other electrical devices which may be found desirable at a later date. The wiring should also take into consideration the probable consumption of the electrical equipment which may be used; if it is considerable, the line should be separately fused so that, if overloaded, the entire house will not be thrown in darkness. The wiring diagram may well include also a ceiling light for general illumination operated from a switch to one side of the door.

Illumination.—In Fig. 304 are shown four types of safelight lamps: (*a*) is designed primarily for use in side wall fixtures, (*b*) for use on a drop cord over the sink or workbench, (*c*) for wall mounting, while (*d*) is suspended by chains from the ceiling to provide general illumination over the room. Safelight screens[1] are readily changed in all of these lamps except the last; in this case, a double lamp may be had, one-half of which is fitted with a safelight screen for film and the other for paper.

A safelight is a color screen which, when used in conjunction with a suitable light source, provides illumination by which a particular sensitive material may be handled with reasonable safety. To this end it must, as far as is consistent with a suitable visual intensity, transmit only illumination within the wave length region to which the emulsion is least sensitive. Any safelight then is necessarily a compromise between two conflicting requirements, maximum safety and maximum visibility, which last depends upon the amount of light transmitted and its wave length region.

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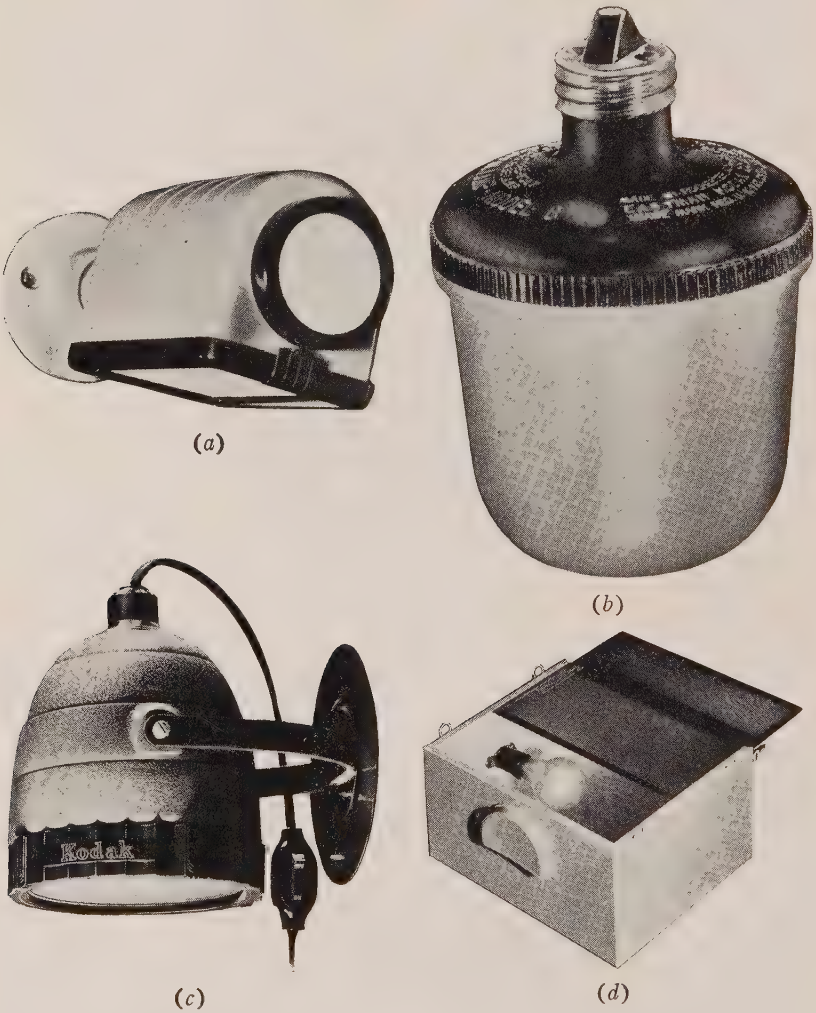
[1] Safelight screens for various types of negative materials, p. 525.



(a) (b) (c) (d)

Fig. 304. Typical Safelight Lamps.

Mees and Baker—Phot. J. **47** (1907) 276. Chilton, Phot. J. **71** (1931) 226.

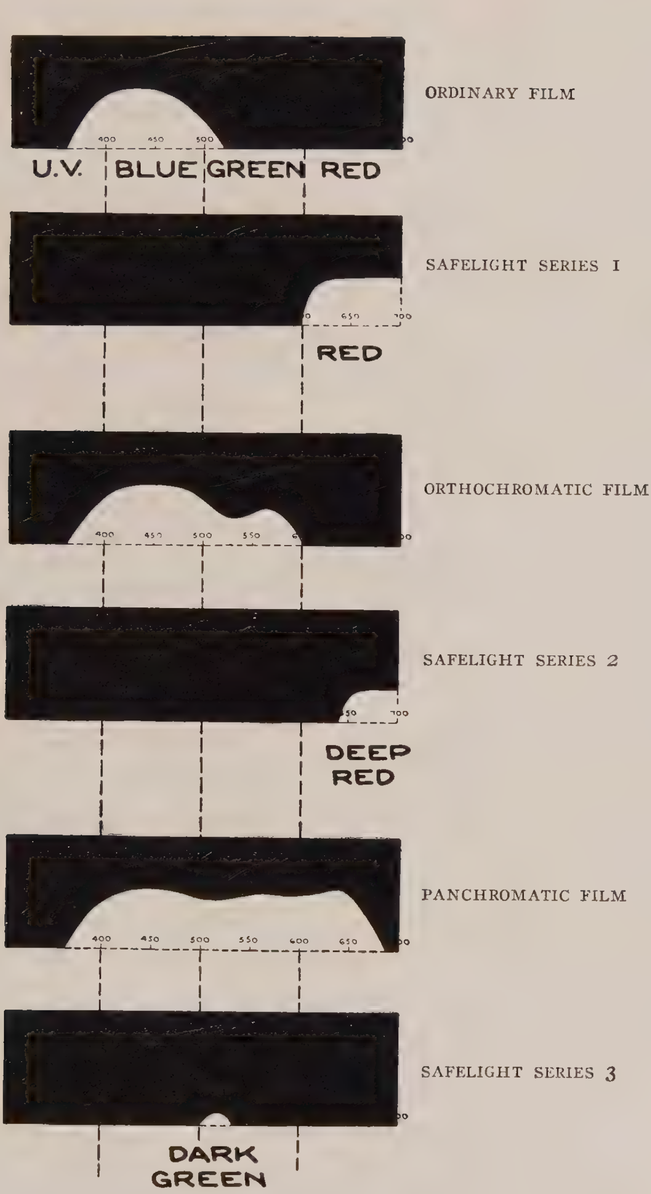


Fig. 305. Spectrograms of Safelights for Use with Different Types of Sensitive Material. (Wratten Safelights, Eastman Kodak Co.)

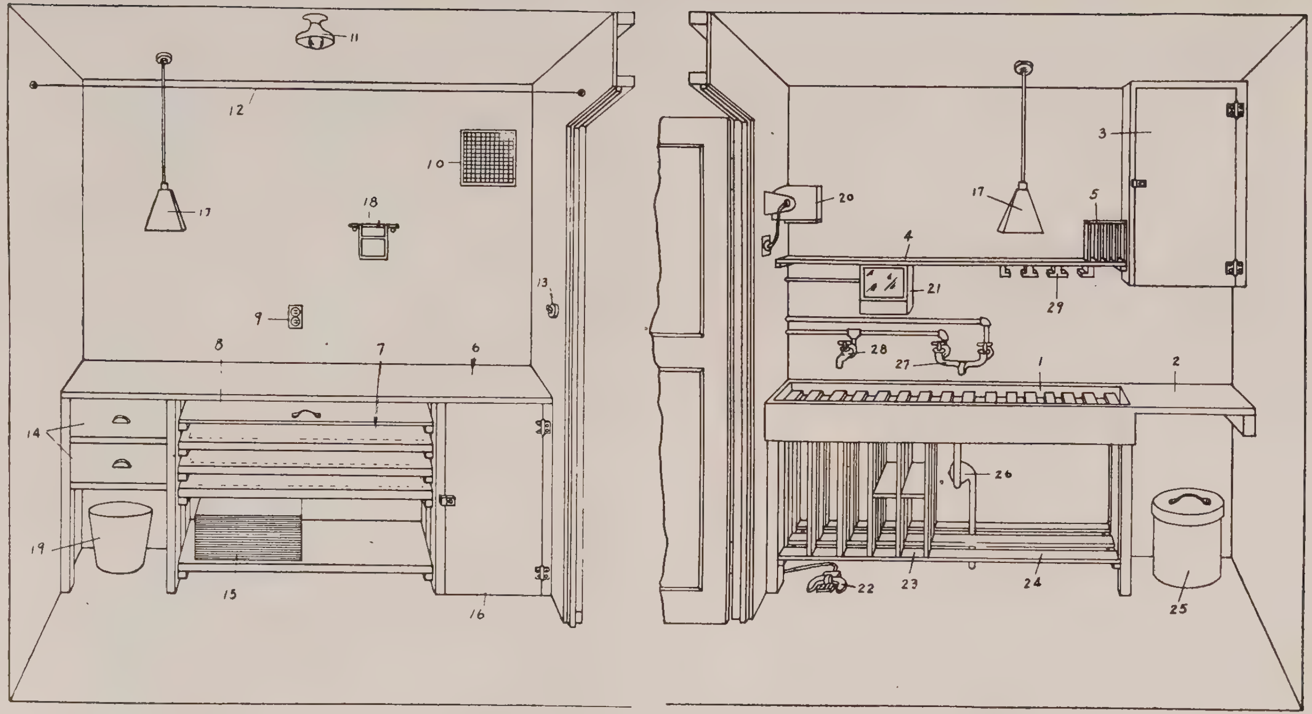
A safelight transmitting red only is satisfactory for blue-sensitive and medium speed orthochromatic materials since both are practically insensitive beyond a wave length of 550 $m\mu$ (Fig. 305). With high-speed orthochromatic materials a safelight transmitting only the extreme red (Fig. 305) provides a greater margin of safety without too great a sacrifice in illumination.

Panchromatic materials are sensitive throughout the visible spectrum so that it is obviously impossible for a safelight transmitting any part of the visible spectrum to be really safe. The problem in designing a safelight for such materials is to obtain the maximum visibility with the smallest possible amount of light. The eye is not equally sensitive throughout the spectrum and at low intensity levels the blue-green region affords the maximum visibility for a given amount of light.

The sensitiveness of super-sensitive and hyper-sensitive panchromatic plates and film is so great that no light which is of any real value visually is safe while the emulsion is dry. When partly developed, its sensitiveness is lower and the safelight may then be used for momentary inspections of the developed image without serious danger of fog.

The standard of safety adopted for the products of at least one manufacturer of screens is that no effect should be produced on the plate when it is exposed to the safelight at a distance of one meter for thirty seconds. Most screens will produce fog if rapid or highly color-sensitive plates are exposed to their action for much over a half minute. A good working test of safety is to place a plate facing the safelight and about three feet away and expose part of it for thirty seconds, leaving part of the plate unexposed by covering it with several coins, or a piece of black paper. If the plate shows signs of fog, after development in total darkness for the usual time, the light is not safe and either a weaker light source should be used, the plate handled at a greater distance from the lamp, or the safelight should be changed to one affording greater safety.

Arrangement.—The best arrangement of the room depends upon its size, the position of the door, the availability of water and drain lines, the kinds of work to be done, the equipment to be installed and to a considerable degree upon the ideas and personal preferences of the builder. Convenience and efficiency in working should receive careful consideration. There should be sufficient space for the different operations and space which is suitably arranged. For example, the space set aside for contact and projection printing and for the handling of film and paper should be at some distance from the sink, or sepa-



(a)

(b)

FIG. 306. Plans of Darkroom for Advanced Amateur. (Eastman Kodak Co.)

rated from it by a screen, which will protect the sensitive materials from accidental wetting. Fig. 306 shows three views of a darkroom designed for general amateur use by the Eastman Kodak Company. It is reproduced not with the idea that it will be suitable for all individual requirements, or that it will be adaptable to every situation, but because it may offer suggestions of value.

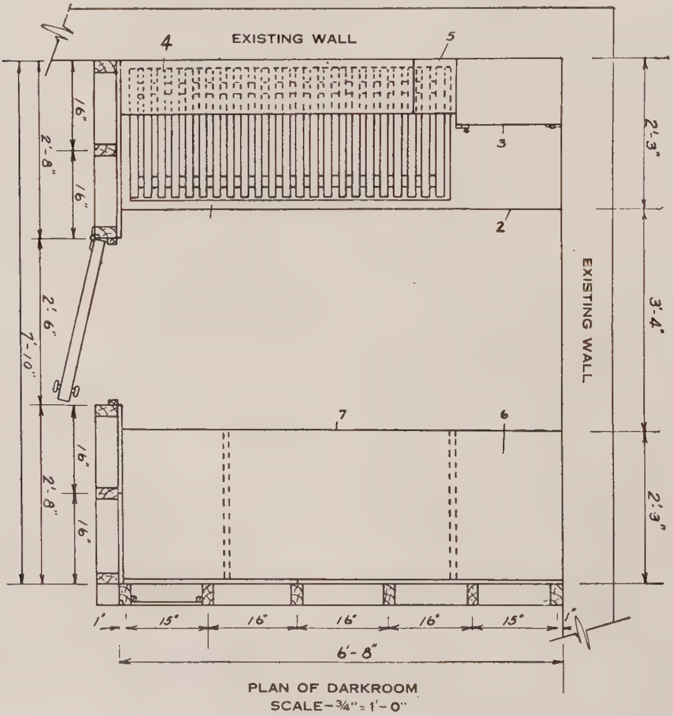


Fig. 306 (*c*).

The Professional Darkroom.—Usually in a commercial business, separate darkrooms for negative processing and printing are desirable, although in a small business, both may be combined. A typical arrangement for the processing of sheet film by the open tank method is shown in Fig. 307. The steel enamel, hard rubber, porcelain or stone tanks accommodate from one to two dozen sheet films on hangers and require from one to five gallons of solution. The tanks on the left are for the developer and those at the opposite end of the sink are for rinsing, fixing and washing as indicated. If warm weather is prevalent

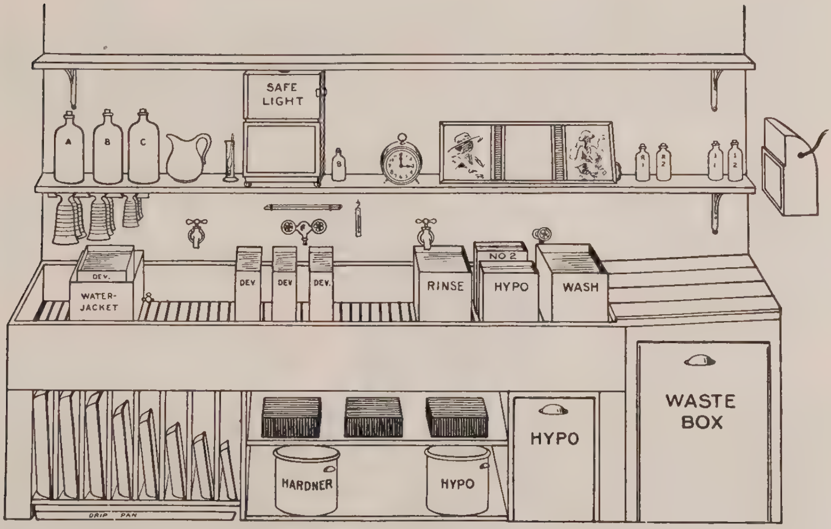


Fig. 307. Darkroom Arrangement for the Processing of Sheet Film in Open Tanks.

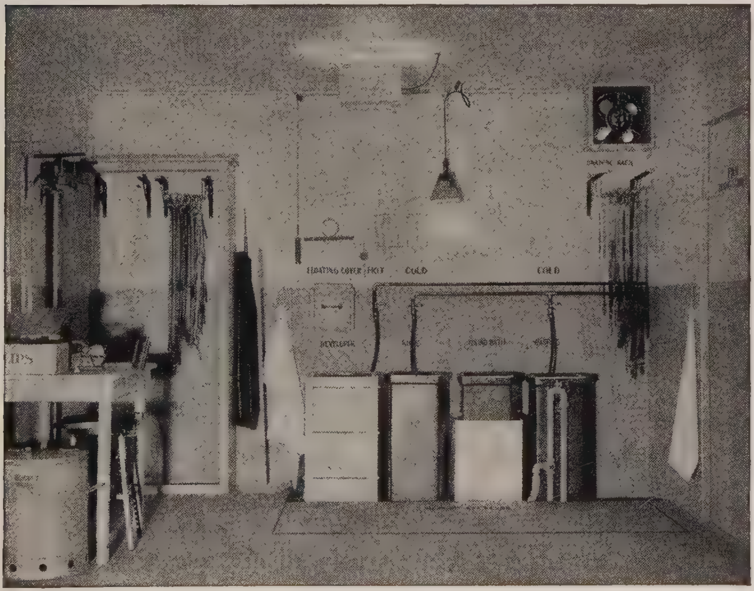


Fig. 308. Deep Tank Installation for Processing Roll Film.

for much of the year, an additional tank for a hardening-stop bath may be placed between the rinsing and the fixing tanks. Usually only the developing tanks are enclosed in a water jacket connected to the cold and hot water taps so that the temperature of the solution may be kept uniform.

A typical deep tank installation for commercial photofinishing is shown in Fig. 308. The films are first separated from their backing papers, numbered, usually with a perforating numbering machine, and attached to a hanger from which they are suspended in the tank for development.

At the expiration of the required time of development, the hanger with its attached films is lifted from the tank and transferred to a rinsing tank through which water from the mains is kept flowing. In some cases, the films are transferred directly from the rinsing to the fixing tank; however, in locations where warm weather prevails for much of the year or films are dried rapidly by heat the rolls are usually first transferred to a tank containing a hardening stop bath of chrome alum and thence to the fixing bath. One or more tanks are employed for fixing and two or more for washing. The films are dried in cabinets with circulating heated air.

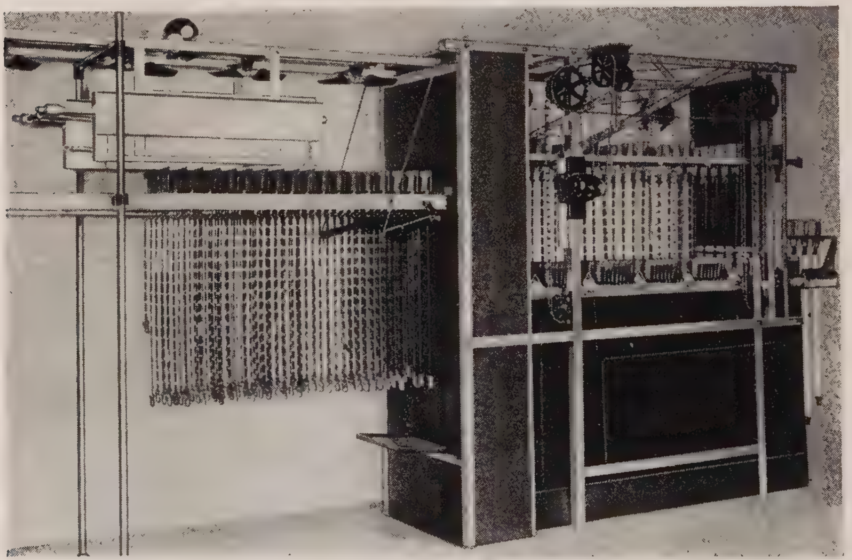


Fig. 309. Pako Filmachine for the Automatic Processing of Roll Film.

In recent years, automatic processing machines have been widely adopted for commercial photofinishing. These consist essentially of overhead conveyor systems which automatically transfer hangers containing the films from one tank to another. A typical processing machine for photofinishing is shown in Fig. 309.

Developing Tanks for Roll Film.—Tank development has become almost universal on account of its greater convenience, economy of time and solution, and lastly, but most important of all, superior results from the standpoint of uniformity and freedom from fog, scratches, and other physical defects.

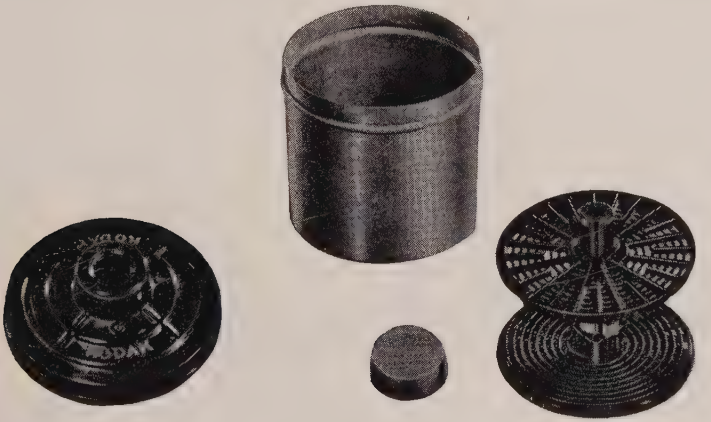


FIG. 310. Tank for the Development of Roll Film.

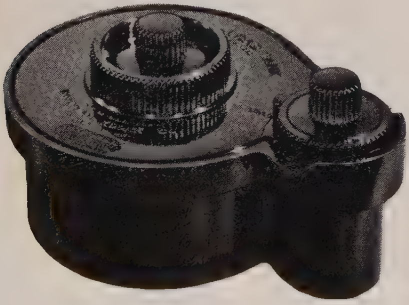


FIG. 311. Day-Load Tank for the Development of 35 mm. Film Magazines in Daylight.

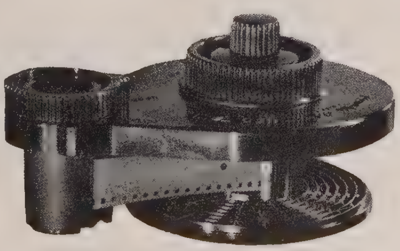


FIG. 312. Interior of Tank Illustrated in Fig. 311, Showing How the Film is Transferred from Magazine to the Tank.

A tank for the development of roll film consists essentially of the tank proper and a spiral reel for holding the film during development. The film is separated from its paper backing and wound on the reel in the darkroom. The film is held in the spiral turns of the reel. The loaded reel is then placed in the tank containing the developer and the cover attached. In some cases, the cover is placed on the tank first and the developer added through a light-tight opening in the top. In this case, the tank may be emptied, the film is rinsed and the fixing solution added before exposing the film to light. While tanks of this type do not enable film to be developed in daylight, since a darkroom is necessary for loading, there is no apron and consequently no danger of markings on the back of non-curling films from contact with the apron during development. This is important in the case of small negatives because such markings sometimes appear in the enlargement. The reel, however, must be designed to permit the free circulation of the developer or it is difficult to avoid uneven development.

In Fig. 311 is shown a developing tank which enables film in 35 mm. daylight loading magazines to be developed in full daylight. The film magazine is placed in the chamber to one side of the tank and the free end of the film projecting beyond the magazine is inserted in the spindle of the developing reel (Fig. 312). The film magazine and developing reel, which together form the cover of the tank, are then placed in the tank and the film wound on the reel by turning the knurled collar at the top (Fig. 311). The empty film magazine is then removed and the developing solution poured in through the opening in the top of the magazine chamber. During development, the agitation necessary for uniform development is obtained by rotating the developing reel by means of the knurled collar at the top of the tank.

Developing Tanks for Sheet Film and Film Packs.—Three types of tanks for the developing of sheet film and film packs are shown in Fig. 313. All of these must be loaded in a darkroom or a changing bag. In (*a*) the films are held parallel to one another in a rack which is adjustable for different sizes; in (*b*) the film with its backing paper is bent double and inserted in the rack as shown. The tank shown in (*c*) is divided into three compartments for developing, fixing and washing. Each tank has a drain and a light proof cover. The films are held parallel to each other in the rack shown at the right which is used for fixing and washing as well as for developing.

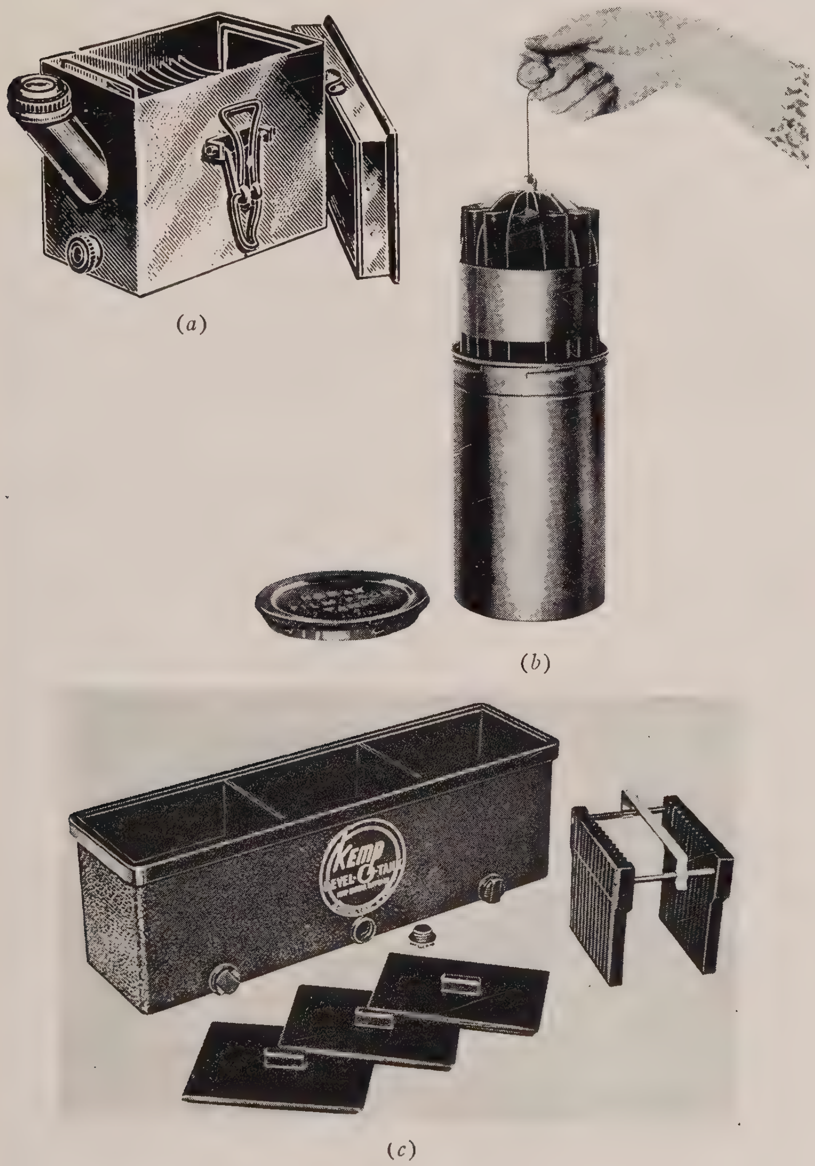


FIG. 313. Tanks for the Development of Sheet Film in Amateur Sizes.

NEGATIVE DEVELOPERS

For purposes of discussion, negative developers will be divided into seven classes:

1. General purpose developers.
2. Fine grain developers.
3. High contrast developers.
4. Two-bath developers.
5. Developers for use at a high temperature.
6. Rapid developers.
7. Physical developers.

In a number of cases these overlap; a long useful life is characteristic of two-bath developers, which may also be designed for use at high temperature or for extremely rapid development, while physical developers may be regarded equally as fine grain developers.

These classes of negative developers will be discussed in the order named.

General Purpose Developers.—A general purpose developer, when used with medium or high speed negative materials, should develop with moderate rapidity, produce good density and contrast, a reasonably fine grain suitable for contact printing and moderate enlargement, a low fog density, keep reasonably well in solution, be non-staining and develop the latent image fully; i.e. require no increase in exposure. Where, for any particular reason, one of these requirements assumes special importance, as in the development of miniature camera negatives which must be greatly enlarged, or when using sensitive materials of the "process" type for copying line drawings etc., it is usually necessary to sacrifice the other desirable qualities and select a *special* purpose developer in accordance with the requirements.

While approximately ten developing agents are in more or less general use for negative development, the combination of metol and hydroquinone greatly exceeds all others in popularity. Included in the table on page 535 are the formulas of a number of metol-hydroquinone developers published by the manufacturers of negative materials and intended for general use.

Fine Grain Developers.—Fine grain developers may be divided into three classes:

1. Metol-hydroquinone, metol-paraminophenol or diaminophenol developers employing a solvent of silver halide such as ammonium chloride, hypo, sodium sulfite, or an alkali thiocyanate.
2. Paraphenylene developers.
3. Paraphenylene-glycin, paraphenylene-metol and other paraphenylene combinations.

GENERAL PURPOSE METOL-HYDROQUINONE DEVELOPERS

	Agfa 48 M		*Defender 3D*		*Kodak Dk 60a*	
Water (125° F. or 52° C.)	750.0 cc.	24 oz.	500 cc.	16 oz.	750 cc.	24 oz.
Metol (Elon)	2.0 gm.	30 gr.	3.1 gm.	45 gr.	2.5 gm.	37 gr.
Sodium Sulfite (des.)	40.0 gm.	1¼ oz. 40 gr.	90.0 gm.	3 oz.	50.0 gm.	1 oz. 290 gr.
Sodium Bisulfite	—	—	2.1 gm.	30 gr.	—	—
Hydroquinone	1.5 gm.	22 gr.	5.9 gm.	85 gr.	2.5 gm.	37 gr.
Sodium Carbonate (des.)	—	—	11.5 gm.	165 gr.	—	—
Sodium Metaborate	10.0 gm.	¼ oz. 35 gr.	—	—	—	—
Kodalk	—	—	—	—	20.0 gm.	290 gr.
Potassium bromide	0.5 gm.	7.5 gr.	1.7 gm.	24 gr.	0.5 gm.	7½ gr.
Water to make	1.0 liter	32 oz.	1.0 liter	32 oz.	1.0 liter	32 oz.

Agfa 48 M: Use without dilution. Time of development at 65° F. (18° C.) in tray from 4–6 minutes: in tank from 5–7 minutes, depending upon the emulsion, degree of agitation and contrast required.

Defender 3D:

For tray use: Take 1 part of the stock solution to 1 part of water. Time of development from 4–6 minutes at 70° F. (21° C.), depending upon degree of agitation, emulsion and degree of contrast desired.

For tank use: Take 1 part of stock solution to 3 parts of water. Time of development from 9–14 minutes at 70° F. (21° C.), depending upon degree of agitation, emulsion and contrast desired.

Kodak Dk 60a: Time of development from 7–12 minutes at 65° F. (18° C.), depending upon degree of agitation, emulsion and contrast desired.

The reduction in the graininess of the image obtained with developers of class 1 is due probably (*a*) to an actual reduction in the size of the developed grain due to the action of the silver halide solvent on the grain of silver halide in development, and (*b*) a more uniform distribution of the grains of silver in the deposit as a result of development in the presence of a solvent of silver halide becoming largely physical in character.

While a metol-hydroquinone developer containing ammonium chloride was recommended by Lumière and Seyewetz as early as 1904 [2] and with diaminophenol by Lazenby in 1934,[3] the most successful developers of this class have been those employing high concentrations of sodium sulfite or an alkali thiocyanate. The first fine grain developer of the metol-hydroquinone borax type was published by Wellington, but the first to achieve widespread popularity was that of Capstaff, familiarly known as D–76.[4] In developers of this type, borax or a metaborate is used, the lower alkalinity indirectly favoring the solvent action of the sulfite.

Increasing the amount of sodium sulfite, or reducing that of the developing agents, results in some improvement in graininess as does the addition of potassium bromide, but at the expense of effective emulsion speed, necessitating increased exposures and longer times of development. From a practical standpoint, the improvement in graininess is too slight to justify these disadvantages.[5]

Mees appears to have been the first to employ an alkali thiocyanate as a silver halide solvent in a developer, but for the purpose of obtaining colored images on lantern slides rather than for negative development.[6] Strauss suggested the use of sodium thiocyanate for fine grain negative development in 1937 and the following year Crabtree and Henn of the Kodak Research Laboratories published the formula of the first fine grain developer of this type as DK–20. This formula produces images with less graininess than the elon-hydroquinone borax formulas, comparing very favorably in this respect with paraphenylene diamine formulas. The effective emulsion speed is reduced by about 35% which, from a practical standpoint, is negligible and somewhat less than representative paraphenylene diamine developers.

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[2] Lumière and Seyewetz, *Brit. J. Phot.* **51** (1904) 630, 866.

[3] Lazenby, *Brit. J. Phot.* **81** (1934) 663.

[4] Capstaff and Seymour, *Trans. Soc. Mot. Pict. Eng.* **10** (1926) 223.

[5] Crabtree and Carlton, *Trans. Soc. Mot. Pict. Eng.* **38** (1929) 406.

[6] Mees, *British Journal Almanac* 1912, p. 515. The use of thiocyanate was patented: U.S.P. 2,136,968 of 1936. The use of thiourea has also been patented: U.S.P. 2,147,441.

KODAK FINE-GRAIN DEVELOPER (FORMULA DK–20)

Water (about 125° F.) (52° C.)	750.0 cc.	96 oz.
Elon	5.0 gm.	290 gr.
Sodium sulfite, desiccated	100.0 gm.	13¼ oz.
Kodalk	2.0 gm.	116 gr.
Potassium thiocyanate	1.0 gm.	58 gr.
Potassium bromide	0.5 gm.	29 gr.
Cold water to make	1.0 liter	1 gallon

Dissolve chemicals in order given.

Time of development from 14–18 minutes at 65° F. (18° C.) depending upon sensitive material, degree of agitation and negative contrast required.

Developers of paraphylene alone are not widely used despite the exceptionally fine grain of the image because it is obtained at the expense of emulsion speed which is reduced from 25 to 50% of that obtained with developers of the elon-hydroquinone borax type and in some cases even more. In addition, paraphenylene developers are toxic, stain the fingers, trays, etc. badly, develop slowly and it is sometimes difficult to obtain sufficient density and contrast. Developers of greater activity, with shorter times of development, may be obtained with the addition of an alkali, but the graininess increases rapidly with the activity. For these reasons, paraphenylene is usually used in combination with other developers of greater energy, such as metol, glycin or meritol. Of the many such "compromise" formulas, those of Sease, Lowe and Champlin are perhaps the most popular.[7]

PARAPHENYLENE DEVELOPERS (2)

Dupont N.D. 3

Water 125° F.	975.0 cc.	30 fl. oz.
Sodium sulfite (des.)	90.0 gm.	3 oz.
Paraphenylenediamine	10.0 gm.	146 gr.
Glycin	2.0 gm.	29 gr.
Water to make	1.0 liter	32 fl. oz.

Use full strength. Develop 15–30 minutes at 65° F.

[7] Sease, *Camera* (*Phila.*) **47** (1933) 1. Lowe, *Zeiss Magazine* **2** (1936) 75. Lowe, *Camera Craft* **43** (1936) 558. Champlin, *Champlin on Fine Grain.* Camera Craft Publishing Co. 1937.

Harris—M.C.W. 100; An Entirely New Formula for Super-Fine Grain Development. Miniature Camera Mag. **2** (1938) 236.
Mudrovčić—Tests of Fine Grain Developers. Brit. J. Phot. **86** (1939) 74.
Seyewetz—Redevelopment for Fine Grain. Brit. J. Phot. **86** (1939) 186.
Seyewetz—Orthophenylene diamine for Fine Grain Development. Brit. J. Phot. **83** (1936) 487.
Schilling and Dehio—Tests of Fine Grain Developers. Phot. Ind. **34** (1936) 167.
Vittum (Eastman Kodak Co.)—Fine-Grain (Non-Fogging) Photographic Developer. U.S.P. 2,113,312, 1935.

FINE GRAIN DEVELOPERS

	Agfa 17-M		Defender 6D		Kodak D-76	
Water (125° F. (52° C.)	750.0 cc.	24.0 oz.	750.0 cc.	16 oz.	750.0 cc.	24 oz.
Metol	1.5 gm.	22 gr.	2.0 gm.	32 gr.	2.0 gm.	29 gr.
Sodium sulfite (des.)	80.0 gm.	2½ oz.	98.0 gm.	3⅓ oz.	100.0 gm.	3 oz. 14.5 gr.
Hydroquinone	3.0 gm.	45 gr.	5.0 gm.	75 gr.	5.0 gm.	73 gr.
Borax	——	——	2.0 gm.	75 gr.	2.0 gm.	29 gr.
Metaborate	2.0 gm.	30 gr.	——	——	——	——
Potassium bromide	0.5 gm.	7½ gr.	——	——	——	——
Water to make	1.0 liter	32 oz.	1.0 liter	32 oz.	1.0 liter	32 oz.

Agfa 17-M: Use without dilution. Time of development at 65° F. (18° C.) from 10–15 minutes, depending upon the emulsion, degree of agitation and contrast required.

Defender 6D: Use without dilution. Time of development at 70° F. (21° C.) from 5- 20 minutes, depending upon the emulsion, the degree of agitation and the contrast required.

Kodak D-76: Use without dilution. Time of development at 65° F. (18° C.) from 10–25 minutes, depending upon the emulsion, the degree of agitation and contrast required.

PARAPHENYLENE DEVELOPERS FOR FINE GRAIN

	Sease No. 3		*M.C.W. 100*		*Edwal*[9]	
Water	1 liter	32 oz.	1 liter	20 oz.	1 liter	32 oz.
Metol	—	—	—	—	6 gm.	90 gr.
Sodium sulfite (des.)	90 gm.	3 oz.	88 gm.	1¾ oz.	90 gm.	3 oz.
Paraphenylenediamine	10 gm.	150 gr.	—	—	10 gm.	150 gr.
Glycin	6 gm.	90 gr.	—	—		
Meritol			16 gm.	140 gr.		
Borax			2.3 gm.	20 gr.		
Trisodium phosphate			6.9 gm.	60 gr.		
Potassium bromide			(10%) .2 cc.	20 min.		
Glycin	—	—	—	—	5 gm.	75 gr.

Champlin 16		
Sodium sulfite (des.)	50 gm.	1⅔ oz.
Chlorohydroquinone	25 gm.	¾ oz.
Teronamin C	30 cc.	1 oz.
Water	500 cc.	16 oz.

For use, dilute one part with 9 parts of a 10% solution of sodium sulfate.

Champlin 17[8]		
Elon	0.70 gm.	10 gr.
Sodium sulfite (des.)	104.5 gm.	1465 gr.
Diethyl glycol	1.3 cc.	25 min.
Trilthylanolamine	1.56 cc.	30 min.
Chlorohydroquinone	15.4 gm.	50 gr.
Water	1 liter	32 oz.

Use without dilution. Time of development is from 5½ to 6½ minutes at 70° F. according to the contrast desired.

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[8] Champlin 17, *Minicam* **3** (1940) April 32.

[9] Lowe, *Developers, Fine Grain and Otherwise.* Camera Craft Publishing Co., San Francisco 1939.

Rapid Development.—Two bath developers are particularly well adapted to high speed processing since the degree of development is under better control than with the usual single solution developer. The Agfa two solution developer, and the Kodak formula SD–6 on page 542 are rapid developers for use at temperatures up to 80° F. (25.5° C.) but formula SD–4 is not. A two-bath developer which is said to produce satisfactory results in ten seconds consists of a 5% solution of hydroquinone with 2% sodium sulfite followed by a 30% solution of potassium hydroxide. The times of immersion are eight seconds in the first bath and two in the second at a temperature of 80° F. (26.7° C.). The time of immersion in the second bath should not exceed a few seconds or the gelatin may be softened and reticulation produced.[10]

For development within 30 seconds to one minute, the following single solution metol-hydroquinone developer has been recommended: [11]

Elon or metol	15 gm.	65.6 gr.
Hydroquinone	15 gm.	65.6 gr.
Sodium sulfite (des.)	50 gm.	219.0 gr.
Sodium hydroxide	20 gm.	87.5 gr.
Potassium bromide	1 gm.	4.4 gr.
Water to	1 liter	10.0 oz.

Use full strength.

For temperatures above 85° F. (30° C.), the sodium hydroxide is reduced to 10 grains and the potassium bromide increased to 8 grains to reduce fog.

With this developer in particular and with rapid developers in general, a 3% acetic acid stop bath to arrest development and prevent excessive contrast and fog is desirable.

Two-Bath Development.—Methods of developing involving the use of two separate baths may be divided into three main classes:

Class I: Those in which the first bath contains all of the developing agents plus sodium sulfite and the second the alkali and the remainder of the sulfite.[12]

The gelatin swells and absorbs a certain amount of the developing solution in the first bath but little or no development takes place owing to the absence of the alkali. When the film is transferred to the second bath development proceeds until the developing agents held in the gelatin have been exhausted or have diffused out into the surrounding solution. Developers of this type result in an almost constant degree of development (γ) regardless of the time of development or the temperature of the solution and hence possess certain advantages where a certain fixed degree of development (γ) is desired.

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[10] Starke, *Phot. Ind.* **35** (1937) 308, 310.

[11] Charriou and Valette, *Rev. franç. Phot.* **19** (1938) 205, 208.

[12] von Janovich, *Phot. Korr.* **44** (1907) 359, 505; Knapp, *Brit. J. Almanac* (1932) 191; Crabtree, Parker and Russell, *J. Soc. Mot. Pict. Eng.* **21** (1933) 21; Baker, *Brit. J. Phot.* **56** (1909) 609; **58** (1911) 101.

Two-bath developers of this type have a long useful life. The first bath is changed but little and requires only the addition of fresh solution to replace that carried out by the film. Reaction products which restrain development accumulate in the second bath which must be renewed frequently. The degree of development (γ) remains practically constant during exhaustion.

Class II: Two-bath developers in which both contain the developing agents, sulfite and alkali but in different proportions.

In developers of this type the first bath is designed to serve as a replenishing solution for the second. Since the quantity of the first bath carried over into the second is proportional to the quantity of film processed; if the formula of the first bath is designed to fit the particular conditions of use the rate of development will remain uniform. Two-bath developers of this type, therefore, permit of greater exhaustion than do single bath developers without a corresponding loss in effective emulsion speed or rate of development.

Class III: Two-bath developers of like composition.

A two-bath developer of this type has a longer useful life than a single bath developer since development is begun in a fresh bath and completed in one which is partially exhausted. Investigation has shown that this may be done without loss in effective emulsion speed and without materially affecting the quality of the negative.[13]

The time of immersion in the first bath is short—only long enough for the image to appear—hence, the rate of exhaustion is much less than that of a single bath developer of the same composition. Then, when the second bath is exhausted, the first bath is replaced with fresh solution and it in turn becomes the second bath.

[13] Dundon, *Brown and Capstaff, J. Soc. Mot. Pict. Eng.* **14** (1930) 389.

FORMSTECHER—Development in Two Successive Baths. Phot. Ind. **29** (1931) 683.

TWO-BATH DEVELOPERS

	Agfa		*Kodak SD 4*		*Kodak SD 6*	
Solution 1						
Water	—	—	—		750.0 cc.	24 oz.
Elon or metol	5 gm.	75 gr.	5.0 gm.	21.9 gr.	3.0 gm.	44 gr.
Sodium sulfite (des.)	30 gm.	1 oz.	2.0 gm.	8.8 gr.	25.0 gm.	365 gr.
Hydroquinone	10 gm.	150 gr.	100.0 gm.	437.5 gr.	6.0 gm.	88 gr.
Sugar (granulated)	—	—	100.0 gm.	437.5 gr.	—	—
Sodium bisulfate	—	—	5.0 gm.	21.9 gr.	—	—
Sodium carbonate (des.)					20.0 gm.	290 gr.
Sodium sulfate (des.)					100.0 gm.	3 oz. 145 gr.
Water to make			1 liter	10.0 oz.	1.0 liter	32 oz.
Solution 2						
Phenosafranine (1 : 1000)			—	—	20.0 cc.	5 fl. dr.
Sodium carbonate (des.)	100 gm.	3 oz. 55 gr.	10.0 gm.	43.8 gr.	—	—
Sodium sulfate (des.)	—	—	100.0 gm.	437.5 gr.	50.0 gm.	1 oz. 280 gr.
Potassium bromide	—	—	0.5 gm.	2.2 gr.	2.0 gm.	30 gr.
Potassium iodide	—	—	0.01 gm.	4.4 gr.	—	—
Water	1 liter	32 oz.	1.0 liter	10.0 oz.	1.0 liter	32 oz.
Solution 3						
Formaline			—	—	200.0 cc.	6½ oz.
Water to make			—	—	1.0 liter	32 oz.

Agfa Two Solution Developer: At 65° F. (18° C.) 1 minute 15 seconds in each bath. At 70° F. (21° C.) 1 minute in each bath. At 75° F. (24° C.) 45 seconds in each bath. All times with continuous agitation.

Kodak SD 4: Average time of development: 4 minutes in each solution at 65° F. (18° C.). Do not rinse between baths. For 35 mm. negative film.

Kodak SD 6: For rapid development. For use take equal parts solution 2 and 3 to make second bath. Use first without dilution. To develop: immerse one minute in first solution at temperature from 65° F. to 80° F. (18° to 26.5° C.) and transfer without rinsing to second bath for one minute.

Processing at High Temperatures.—The primary problem in the processing of negative material at a high temperature is to avoid undue swelling of the gelatin with its attendant difficulties, frilling, reticulation, melting, separation from the base, etc. A secondary but important consideration is developing without producing an undesirable amount of fog or stain. The various methods of processing at high temperature may be divided into three classes.

1. Hardening before processing.
2. Hardening in development.
3. Prevention of swelling in development followed by hardening in a separate bath after development and before fixation.

Processes based upon hardening before development. The most satisfactory substance for hardening prior to development is formalin (40 percent formaldehyde) in alkaline solution or in conjunction with a salt—such as sodium sulfate, citrate or disodium orthophosphate—which has the property of repressing the swelling of gelatin in warm water.[14]

Formalin hardens gelatin in alkaline solutions only and an undeveloped emulsion will soften if placed in a plain solution of formalin.

Methods based upon hardening in development. Under ordinary conditions, pyro and pyrocatechin are the only developing agents having a pronounced tanning action on gelatin. Metol-hydrochinon developers with a smaller than usual amount of sodium sulfite harden gelatin in consequence of the production of insolubilizing oxidation products.[15]

The tanning action produced in such cases is not uniform but varies with the density of the developed image and the developing solutions have poor keeping properties.

The addition of formalin to many developers results in strong fog and stains. Fogging may be reduced by the addition of a desensitizing agent such as phenosafranine or pinakryptol and by increasing the amount of soluble bromide. A two-bath developer, one bath containing the developers, the other the alkali and hardener is particularly advantageous for developing at high temperatures because under such conditions it is possible to use formalin without the troublesome reactions that occur between formalin and the developing agents in a single bath developer.[16]

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[14] The use of formalin and such salts for hardening is protected by British Patent 128,337 (*Brit. J. Phot.* **66** (1919) 460).

[15] Lumière and Seyewetz, *Brit. J. Phot.* **75** (1927) 134.

[16] Parker and Crabtree, *Amer. Phot.* (1936) 67, 142.

Processes based upon the prevention of swelling during development followed by permanent hardening. The swelling of the gelatin during development may be reduced (1) by using concentrated developers and (2) by increasing the concentration of the developing solution through the addition of inert material such as sodium or potassium sulfate, glucose or sugar. The use of a concentrated developer, to reduce the time of development, and the addition of sodium sulfate, to prevent abnormal swelling of the gelatin, enables development to be conducted satisfactorily at temperatures of 75° F. (24° C.) to 90° F. (32° C.) if the film is permanently hardened in the following chrome-alum, sodium sulfate stop bath immediately after developing and before fixing.[17]

Water	1.0 liter	32 oz.
Potassium chrome alum	30.0 gm.	1 oz.
*Sodium sulfate, desiccated	60.0 gm.	2 oz.

* If it is desired to use sodium sulfate, crystals instead of desiccated, then 3½ ounces per quart (105 grams per liter) should be used.

Agitate the film for 30 to 45 seconds when first immersing it in the hardener, or streakiness will result. The bath is a violet-blue color by tungsten light (white bulb) when freshly mixed, but it ultimately turns a yellow-green with use; it then ceases to harden and should be replaced with a fresh bath. Allow from three to four minutes for hardening and then transfer to the usual fixing and hardening bath.

Regardless of the method employed in processing photographic materials at a high temperature, it is important that the temperature of the various solutions be kept as nearly alike as possible. The transference of the film from a cold solution to a warmer one, or vice-versa, subjects the gelatin layer to strain which is likely to result in reticulation. Recent experiments have shown that the excessive graininess of films processed in warm solutions is a mild form of reticulation although not

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[17] The use of sodium sulfate and similar substances as an addition to developers for the purpose of preventing the swelling of the gelatin was recommended by Bunel, *Bull. Soc. franç. Phot.* (1910) 174; *Brit. J. Phot.* **57** (1910) 399, by Lumière and Seyewetz; *Brit. J. Phot.* **58** (1911) 137, and Eastman Kodak Co.; *Brit. J. Phot.* **71** (1924) 762.

JAENICKE—Shortening the Development Time of Photographic Negatives. Phot. Ind. **35** (1937) 514, 540.

LUMIÈRE AND SEYEWETZ—Developers for Hot Climates. Phot. Rund. **63** (1926) 491.

immediately recognizable as such. The effect of a sudden change in temperature is at a maximum with swollen gelatin, hence, the desirability of preventing swelling at all stages of processing and hardening the film permanently as soon as possible.

DEVELOPERS FOR USE AT HIGH TEMPERATURE

TROPICAL DEVELOPERS

	Agfa 64		*Kodak D 91*	
Water 125° F. (52° C.)	750.0 cc.	24 oz.	750.0 cc.	24 oz.
Metol	2.5 gm.	36 gr.		
Paraminophenol hydrochloride	——	——	7.0 gm.	100 gr.
Sodium sulfite (des.)	25.0 gm.	¾ oz. 40 gr.	50.0 gm.	1 oz. 290 gr.
Hydroquinone	6.5 gm.	95 gr.		
Sodium carbonate (des.)	15.0 gm.	½ oz. 15 gr.	50.0 gm.	1 oz. 290 gr.
Potassium bromide	1.0 gm.	15 gr.		
Water to make	1.0 liter	32 oz.	1.0 liter	32 oz.

Agfa 64: Use without dilution. Develop from 2 to 4 minutes at 65° F. (18° C.); 2 to 3 minutes at 85° F. (29° C.).

Kodak D 91: Use without dilution. Average time of development 7 to 9 minutes at 65° F. (18° C.) and 3 to 4 minutes at 80° F. (26.5° C.). At temperatures above 80° F. add 1½ ounces sodium sulfate per 32 oz. solution (45 grams per liter).

Contrast Developers.—A developing solution designed for maximum contrast with process materials must produce density readily and be free from any tendency to fog even with prolonged development. At the present time, this condition is most nearly satisfied by concentrated metol hydroquinone or hydroquinone developers with a high concentration of alkali restrained with potassium bromide. To secure the high alkalinity necessary for rapid development, the alkaline carbonates are frequently replaced by the caustic alkalis, such as sodium or potassium hydroxide, while for certain sensitive materials the use of para-formaldehyde is recommended. Developers of this type should act rapidly so that full density is produced before the restraining effect of the potassium bromide is overcome.

From a practical standpoint, it should be noticed that developers of this type should not be used at temperatures below 60° F. or above 70° F. Also, to prevent stain, the negative should be rinsed well between development and fixing.[18]

[18] Southworth, *Brit. J. Phot.* **75** (1928) 680, 706.

CONTRAST DEVELOPERS

	Agfa 90		*Kodak D 8*		*Kodak D 11*	
Water 125° F. (52° C.)	750.0 cc.	24 oz.	3.0 liter	96 oz.	500 cc.	16 oz.
Metol or Elon	5 gm.	75 gr.	—	—	1.0 gm.	15 gr.
Sodium Sulfite (des.)	40 gm.	1¼ oz. 40 gr.	360.0 gm.	12 oz.	75.0 gm.	2½ oz.
Hydroquinone	6 gm.	88 gr.	180.0 gm.	6 oz.	9.0 gm.	130 gr.
Sodium carbonate	40 gm.	1¼ oz. 40 gr.	—	—	25.0 gm.	365 gr.
Sodium hydroxide	—	—	150.0 gm.	5 oz.	—	—
Potassium bromide	3 gm.	45 gr.	120.0 gm.	4 oz.	5.0 gm.	73 gr.
Water to make	1 liter	32 oz.	4.0 liter	1 gal.	1.0 liter	32 oz.

Agfa 90: Use without dilution. Time of development 4 to 6 minutes at 65° F. (18° C.).

Kodak D 8: For use take two parts of solution to one part water. Develop 2 to 3 minutes at 65° F. (18° C.). Use not lower than 55° F. (13° C.) or higher than 65° F. Use cold water in dissolving sodium hydroxide (caustic soda).

Kodak D 11: Use full strength. Develop 4 to 5 minutes at 65° F. (18° C.). For lantern slide use dilute with an equal part of water.

Physical Development.—The process of development mistakenly known by this term consists in the use as a developer of a solution containing a silver salt in conjunction with a suitable reducing, i.e., developing agent. The reducing agent results in the formation of metallic silver in a colloidal state which is precipitated upon the latent photographic image. Thus the image is formed as a result of the deposition of silver from the developing solution and not, as in the usual method of development, by the reduction of the exposed grains of silver halide in the emulsion to metallic silver.

So far as negative development is concerned, physical development is of interest chiefly as a means of obtaining an image of extremely fine grain. With physical development, the grain size of the image is largely independent of that of the emulsion. As applied to the development of transparencies, physical development is notable for the rich, velvety, transparency of the shadows and the unique bluish-black tones, while as a means of intensification it has the advantage of acting proportionally and unlike many other methods of intensification producing permanent results.

Against these advantages must be set certain disadvantages: (1) the process is slow, (2) more than ordinary care and attention to detail is required, (3) there is less latitude in exposure, (4) there is less control over the contrast of the negative.

In 1939, Odell's procedure was improved by McQuown, who added borax to the developer. The formulas and directions which follow are the revised procedure due to McQuown:

Forebath—

Potassium iodide	23.5 gm.	106 gr.
Sodium sulfite (des.)	51.5 gm.	250 gr.
Water to make	1.0 liter	20 oz.

Use full strength. The time of immersion is 40 seconds. Finally rinse for 20 seconds.

Developer (stock solution)—

Sodium sulfite (des.)	96.0 gm.	1 oz. 403 gr.
Silver nitrate, crystal	13.7 gm.	120 gr.
Borax, powdered	13.7 gm.	120 gr.
Sodium thiosulfate	120.6 gm.	2 oz. 180 gr.
Water to make	1.0 liter	20 oz.

The stock solution must be made up carefully by first dissolving the sodium sulfite in water at a temperature of about 120° F. (50° C.). The silver nitrate is then dissolved in about 4 ounces of water at the same temperature. The silver solution is then added, precipitate and all, slowly to the solution of sodium sulfite with vigorous stirring. The borax is then added to the solution and finally the sodium thiosulfate, after which the total volume is made up to 20 ounces or 1 liter. The solution should be allowed to stand for 12 hours before use and filtered with Whatman No. 2 filter paper.

The working solution is made up as follows directly before use:

Stock solution	250 cc.	1 oz.
Water to make	750 cc.	4 oz.
Diaminophenol	2.75 gm.	6 gr.

The time of development depends upon the sensitive material and the contrast required but varies from 12 to 20 minutes at 65° F. (18.5° C.). It is best to develop wholly by time as the image appears to be lacking in density and contrast until after it has been fixed, so that it is difficult to follow development by inspection.

After development, the film is rinsed briefly and fixed in an acid hardening and fixing bath in the usual way.

Horizontal Development.—This term is applied to a method of development advocated by Walter in 1907, in dealing with negatives of contrasty subjects. The tray is made absolutely level, the development solution poured over the plate or film and *left undisturbed until development is complete.* Sensitometric studies of the results obtained have been made by Mees and Wratten and by Heydecker. The latter, using a dilute glycin developer requiring 50 minutes to develop, found that the lower densities—those lying in the toe of the D log E curve—are increased, while the higher densities are depressed and the shoulder of the curve begins at a lower density.

The developing tray must be absolutely level and the solution totally undisturbed during development if the end sought is to be attained. The theory of this method of development is that those portions of the negative which have received the most exposure develop first and

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McLaren—Physical Development. Brit. J. Phot. **85** (1938) 464.
McQuown—Physical Development. Brit. J. Phot. **85** (1938) 446.
McQuown—A Method of Physical Development. Brit. J. Phot. **86** (1939) 470, 483, 499.
Odell—After Four Years of Physical Development. Brit. J. Phot. **84** (1937) 310.
Turner—Physical Development in Practice. Brit. J. Phot. **85** (1938) 403.
Turner—A Year's Work on Physical Development. Minature Camera World, Feb. 1939, p. 127.

release free bromide which, owing to the stagnant developer, remains in the vicinity where it is created and serves to retard development, thus preventing the highlights from attaining their full density, while the lower densities are being fully developed.

In the P and H process developed by Frank Perry,[19] the film is first immersed in a concentrated developer removed soon after the image has appeared, squeegeed to a glass plate, and then placed in water at a temperature of 70° until development has been completed.

A modification of this process suggested by Knapp[20] consists in alternate immersion of the film in developer and in water. The developer recommended by Knapp contained 2 grains of diaminophenol and 10 grains of sodium sulfite per ounce of water, but other developers can be used; in metol-hydroquinone developers, however, the hydroquinone should be replaced by chloro-hydroquinone or aerial fog may be obtained.

The Time of Development.—The time of development is determined by (1) the degree of development, or γ, desired and (2) by the time of development required under given conditions to reach that gamma.

The effect of increasing the degree of development, or γ, is to increase the density scale, or contrast, of the negative, hence, the degree of development depends upon the density scale desired in the negative. This in turn depends upon:

1. *The exposure scale of the paper.* The longer the exposure scale of the paper (lower contrast) on which the print is to be made, the greater the range of density required in the negative.

[19] Perry, *The P & H Process,* Camera Craft Publishing Company, San Francisco, California.

[20] Knapp, *Brit. J. Phot.* **80** (1933) 191.

Knapp—Knapp System of Development. Brit. J. Phot. **80** (1923) 191.

Mees and Wratten—Brit. J. Phot. **54** (1907) 172. Heydecker, Brit. J. Phot. **70** (1923) 635.

Walter—Brit. J. Phot. **54** (1907) 884.

Water-Bath Development (Editorial Comment). Brit. J. Phot. **81** (1934) 422.

Robinson—Some Notes on Water-Bath Development. Brit. J. Phot. **82** (1935) 728.

Smethurst—Knapp Development—Watkins Development Ratings. Brit. J. Phot. **80** (1933) 129.
(Adaptation of the Knapp method of Water-Bath development to time development by the Watkins Thermo method.)

2. *The manner of printing.* Projection printing tends to increase the contrast of the print particularly if condensing lenses are used, so that, in general, negatives should have rather less contrast for projection printing than for contact printing.

3. *The brightness range, or contrast, of the subject.* As the brightness range of the subject increases, the degree of development, or γ, required to produce any given range of densities in the negative becomes less and less. Thus, assuming that the print is to be made on a particular printing paper, negatives of subjects having an extended brightness range such as landscapes including figures beneath trees and open sky, snow scenes with dark objects or shadows near the camera and many interiors, require a lower gamma than subjects of low contrast, as for example, open landscapes, ordinary landscape on dull day, water and sky, old and weatherbeaten buildings in dull light, athletic events in the open, etc.

The time of development required to reach any given gamma depends upon:

1. *The developer.* This involves (1) the formula and (2) its previous history; i.e. whether fresh or used and, in case of the latter, the degree of exhaustion.

2. *The conditions of development.* Included under this head, are such factors as degree of agitation and temperature.

3. *The developing speed of the film or plate.* Sensitive materials differ considerably in the time of development required to attain a given stage of contrast. Information on this subject may be obtained from the Burroughs Welcome Diary and Exposure Guide, published annually, and in the instruction booklets published by the manufacturers of sensitive materials.

Determining Developing Time by Inspection.—The time of development required to obtain a negative having a suitable density scale may be determined by visual examination of the image from time to time during development. However, satisfactory results can be obtained by this method of developing only if one has acquired the ability (1) to recognize the density-scale required and (2) to make the proper allowances for (*a*) the dim light of the safelight lamp and (*b*) the effect of the undeveloped silver halide, which increases all the densities of the image but reduces the density differences, or contrast, and is the cause of the "fixing back" (i.e., loss of density upon fixation) which is so disconcerting to one developing by inspection for the first time.

Development by inspection is thus a matter of judgment based upon experience. As such it is not an ability which can be expressed in terms which convey a definite meaning to another; it must be acquired through practice. One suggestion, however, can be made; the density relationships of the partially developed negative are more readily estimated if it is held with the body of undeveloped halide (i.e., the back of the film or plate) away from the safelight facing the observer.

As it is absolutely necessary to expose the plate or film to the direct rays of the safelight for at least a few seconds in order to follow the progress of development, it is obvious that there is real danger of fog with high speed materials unless desensitized. With supersensitive and hypersensitive panchromatic plates and films exposure to light of any kind during development is inadvisable and development by inspection is really practical only if a desensitizer is employed.

Factorial Development.—The relation between the time of appearance of the image and the time of development is sometimes called the *arithmetical coefficient of development,* or more frequently the Watkins factor, after Alfred Watkins who developed a method of determining the time of development based upon this relationship (factorial development).

For a constant gamma, the factor depends chiefly upon the developing agent and is not altered by temperature, by variations in the proportion or nature of the alkali employed, nor the dilution,—except in the case of pyro and diaminophenol. In general, the factor does not change for different emulsions except with some few which contain a large percentage of iodide.

The factors for a few of the common developing agents are as follows:

Adurol	5	Amidol (2 gr. to the oz.)	18
Pyrocatechin	10	Rodinal	40
Hydrochinon (min-KBr)	5	Ortol	10
Eikonogen	9	Edinol	20
Glycin (Carb. Soda)	8	Pyro (depending on dilution)	5–15
Glycin (Carb. Potash)	12		
Paramidophenol	16		

With any given developing agent the factor depends upon the degree of contrast, or gamma, which it is desired to reach. Once the factor is found for any given set of conditions the time of development can always be readily determined by multiplying the time of appearance by the proper factor.

As a means of determining the time of development, the factorial method has two disadvantages: (1) the time of appearance, and consequently the time of development, varies with the exposure so that underexposures are overdeveloped and overexposures, underdeveloped; (2) the difficulty of applying the method to color sensitive materials due to the danger of fog if the safelight is sufficiently bright to enable the first appearance of the image to be observed accurately. With panchromatic and highly sensitive orthochromatic materials, factorial development is practical only if the film or plate is first desensitized.

Time Development.—Development by time was largely the outgrowth of the photochemical investigations of Hurter and Driffield. Ferguson and Howard investigated the rate of development at different temperatures and Alfred Watkins did much to render the method popular by his carefully compiled tables of the time of development at various temperatures for different films and plates.

Development by time does not depend upon acquired skill in the estimation of the density-range of a negative, nor on observing the time of appearance of the image.

Since visual examination of the image is unnecessary at any stage, time development is the only really satisfactory method in the case of panchromatic materials of extreme sensitivity (unless desensitized), in machine processing and to a lesser degree in large-scale processing by any method.

Development for a fixed time based upon the time required for a given gamma, however, does not allow for variations in the developer, in the developing time of different batches of the same plates or film, the degree of agitation nor variations in the time of development, required with different subjects to produce negatives suitable for a particular paper.

Tables indicating the time of development for a given contrast on plates and films of their own manufacture in certain recommended formulas are published by most manufacturers of sensitive materials.[21] In some cases, developing times are given for different gammas but little or nothing has been published on the gamma to which the negative of a given type of subject should be developed to be suitable for a particular printing paper. This difficulty is largely overcome in practice by selecting a paper with an exposure scale which is suitable for the negative. If the negative must be developed so as to produce the desired result on a particular paper one can do more for himself through a few systematic, carefully planned and well conducted experiments than others can do for him.

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[21] Also in the Burroughs-Wellcome *Handbook and Exposure Guide,* Burroughs-Wellcome Ltd., New York and the *Thermo Development Chart,* American Photographic Publishing Co., Boston, Mass. *Photo-Lab. Index,* Morgan and Lester, New York.

Fixing and Washing.—The fixing and washing of negative materials is discussed in Chapter XI. The paragraphs which follow deal more particularly with special processes.

Hardeners for Use after Washing.—Where a negative is expected to receive considerable handling and may as a result accumulate a goodly number of scratches and abrasion marks, it is well to harden the gelatin thoroughly in a special hardener or "scratchproofing" solution. These solutions produce a hard, glossy surface which resists scratches and abrasion to a considerable degree. A typical formula is:[22]

Tannic acid	25 gm.	¼ oz.
Hot water to	900 cc.	9 oz.
When cold and the solution is clear, add:		
Formaline (40%)	100 cc.	1 oz.

For use, dilute one part of the above to fifteen parts of water. Immerse the clean grease-free negative in this solution for five minutes, wash briefly and dry.

The following chrome-alum formaldehyde formula is recommended for negatives to be dried quickly by heat:

Chrome alum	125 gm.	1¼ oz.
Water (125°)	1.0 liter	10 oz.
Potassium metabisulfite	3.4 gm.	15 gr.
When cold and the contents completely dissolved, add:		
Formaldehyde (40°)	400.0 cc.	4 oz.

For use, take one part of the above to fifteen parts of water, remove any deposit from the wash water or fixing bath adhering to the negative with a viscose sponge, wet absorbent cotton or chamois and immerse in the hardening solution for five minutes. Then wash for a few minutes and dry.

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[22] Willcock, *Brit. J. Phot.* **87** (1940) 65.

Mees and Wratten—Development by Time. Brit. J. Phot. **57** (1910) 376; Phot. J. **50** (1910) 403.

Watkins—Testing the Developing Speed of Plates. Brit. J. Phot. **68** (1921) 383.

The irritating vapors of formaldehyde may be avoided by the use of trioxymethylene (polymerised formaldehyde).[23]

Sodium carbonate (dry)	6.8 gm.	30 gr.
Trioxymethylene	3.4 gm.	15 gr.
Water to	1.0 liter	10 oz.

This is used full strength in the same manner as the previous formula.

Drying.—Upon being removed from the washing tank, the surfaces of the negative should be wiped carefully with a wet viscose sponge, chamois or absorbent cotton to remove dirt and slime which may have become attached to the film and to prevent the formation of drops of water which result in drying marks due to the difference in the time required to dry.

Rapid Drying.—Drying by heat cannot be forced by raising the temperature, or decreasing the relative humidity of the air, because for trouble-free drying, it is necessary that the water be removed more or less uniformly throughout the emulsion layer while, under the conditions just described, the warm air removes the surface water but that within the emulsion layer must be removed by the slower process of diffusion to the surface. Under these conditions, a strain may be set up in the gelatin layer which tends to increase the graininess through the redistribution of the clumps of silver grains to still larger aggregates and, if considerable, may lead to reticulation, frilling, blisters and excessive curling of the film base.

McCutcheon[24] has found that negative materials may be safely dried within three to five minutes, if the surface water is first thoroughly removed with a viscose sponge or chamois, by the infra-red radiation from carbon filament drying lamps. The heat rays from lamps of this type are within a wave length region which is strongly absorbed by water, but only slightly by the gelatin and film base; consequently, the water is evaporated more or less from the whole of the gelatin layer at the same time and not progressively from top to bottom as when warm air is used. The lamps may be obtained with inside reflectors or may be installed in special aluminum Azak reflectors placed from ten to twelve inches from the film. A fan may be used to advantage to remove the water vapor driven off from the film and thus reduce the time of drying. In designing equipment for negative drying using infra-red producing, drying lamps, the lamps should be placed so as to expose the *surfaces* of the negative uniformly. These lamps dry by exposure to infra-red radiation; they should not be used to heat the air in contact with the film as when drying by heat from other sources.

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[23] Crabtree and Russell, B.P. 466,897 (1937) I. G. Farbenindustrie A. G. Use of an organic colloid with polyacrylic acid methyl ester and the like as a hardener.

[24] *Amer. Phot.* **34** (1940) 16. Drying lamps are now obtainable in sizes ranging from 250 to 1000 watts. *The Magazine of Light* **3** (1940) 16.

Another method of drying negatives rapidly is through the use of liquids which displace the water and evaporate more rapidly. Either ethyl or methyl alcohol may be used, but the former is preferable in the case of films as methyl alcohol attacks the base. Acetone is open to the same objection. The milky appearance which is produced occasionally with ethyl alcohol may be avoided by the addition of 1% glycerin or salicylic acid.[25]

The use of heat for drying may lead to a general opalescence due to the dehydration of the gelatin and may be removed by immersing the negative in water and drying normally. The whitish deposit caused by the presence of lime in the wash water, however, cannot be removed without danger to the negative.

Concentrated solutions of certain salts which are highly soluble in water, as for example, aluminum or sodium sulfate and potassium carbonate, have the property of replacing water in gelatin and may be used for the rapid drying of negatives.[26] Thus, if a wet negative is placed in a saturated solution of potassium carbonate for four or five minutes, the gelatin is almost completely dehydrated and, after blotting off the surplus solution and wiping the surface with a soft cloth, the negative is ready for printing.

This process affords a ready means of drying a negative temporarily so that a few prints may be made for immediate use; when the prints are made, the negative should be placed in a small quantity of the solution which should then be diluted with water and finally placed in running water for ten to fifteen minutes and dried in the usual way. If the negative is placed directly in running water, the gelatin may be disrupted and the negative ruined.

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[25] The use of salicylic acid is protected by D.R.P. 507,021 I. G. Farbenindustrie. *Atelier,* **45** (1938) 158.

[26] Lumière and Seyewetz, *Brit. J. Phot.* **59** (1912) 360.

CHAPTER XIX

DEFECTS IN NEGATIVES

Introduction.—In the pages which follow some of the more common defects in negatives are described together with an explanation of their cause and prevention. Considerations of space prevent the inclusion of all the possible difficulties arising from the improper handling of the camera. In the present chapter, those of most frequent occurrence are discussed as well as those difficulties which arise through the improper treatment of sensitive materials in processing. The chapter has been designed to be convenient for ready reference and consequently the headings have been made sufficiently descriptive of the defect to enable it to be readily identified.

Part of Image Is Out of Focus.—Error in focusing or insufficient depth of field. Using camera swings without a sufficiently small diaphragm.

Blurred Image.—Image not properly focused. Camera moved—image uniformly blurred; subject moved—part of image will be sharp.

Part of Image Cut Off.—View finder does not include the same field as the lens. This is due to bad adjustment but all ordinary view finders are adjusted for an object some distance from the camera and do not include the same field as the lens on nearby objects.

When reversible view finders are used, trouble frequently arises from using the vertical portion of the finder for a horizontal picture and vice versa.

Dark Circle in Center of Negative.—Shutter opened with the camera closed.

Tangle of Lines.—Pinhole in bellows. Less frequently in camera front.

Double Image.—Accidental double exposure. Small opening in front of camera. Failure to wind film after exposure (roll film). Shutter may not completely close.

Lack of Sharpness.—Plate or film holder does not register with ground glass. Ground glass reversed. Mirror out of register (Reflex). Marginal unsharpness—film not lying flat in focal plane.

Clear Spots.—Dust in camera. Brushing off films before loading in cut-film holder electrifies the base and causes dust to be attracted.

Fine Parallel Lines (on roll film).—Scratching of the emulsion from some sharp object in camera. Possibly grit. Pinhole in blind of focal-plane shutters.

Bright Objects Are Surrounded by a Vignetted Margin of Great Density.—Halation (see p. 384). Lens not clean.

Clear Band Across One Side of the Negative.—

1. Failure to completely withdraw slide of holder.
2. Cut-off by bellows.
3. Film tab of previous exposure not completely withdrawn (film pack).
4. Baseboard of camera in view (occurs only with wide-angle lenses when focused from the front).

Errors in Exposure and Development.—An underexposed negative is lacking in density and in shadow detail. If the degree of underexposure is slight, detail may be present in even the deepest shadows but does not have the contrast required for good printing quality. The contrast of the negative as a whole may be either low or high depending upon the subject and the degree of development.

An overexposed negative is dense and the contrast of the negative as a whole, and particularly the shadow portions, is less than that of a properly exposed negative. The lack of contrast is particularly noticeable if the time of development has been shortened to prevent the density from becoming too great.

Errors in exposure may be due to:

1. An error in estimating or measuring the brightness of the subject;
2. In making the proper allowance for the color of the subject or the nature of the light source;
3. In setting the diaphragm or shutter speed.

An underdeveloped negative is lacking in contrast and also in density, unless overexposed. Underdevelopment may be distinguished from underexposure by the difference in the contrast of the image. The underdeveloped negative is of lower contrast and has more detail in the shadows.

Overdevelopment results in high contrast and density, particularly in the highlights. Overdevelopment may be distinguished from overexposure by the difference in contrast and the lower density of the shadow portions of the image. Errors in development may be due to:

1. The time of development,
2. The temperature,
3. Variation in the temperature during development,
4. The dilution of the developer,
5. The composition of the developer,
6. The rate of development of the sensitive material.

Fog.—Fog may be due (1) to exposure to light before or during development, (2) to the developer itself, (3) to impurities in the developer, and (4) to exposure of the sensitive material to air during development (aerial or oxidation fog).

Exposure to light before development may arise from a number of sources and may result in either local or general fogging of the image.

Local fogging may be due to:

1. Opening in bellows or front of camera admitting light.
2. Reflection from bright metal parts in camera.
3. Opening between the back of the camera and the film or plate holder, the film pack adapter or the roll holder.
4. Inserting the slide of a film or plate holder, or a film pack adapter by the corner, or twisting the paper tab of a film pack when withdrawing.

General fogging may be due to:

1. Exposing the film to an unsafe light when loading, or prior to development.
2. Exposure of the sensitive material to fumes of burning gas, gasoline, turpentine, ammonia, sodium sulfide, etc.
3. May also be due to an opening in the camera admitting light or to reflection of light from the folds of the bellows which have worn smooth through use.

Fog may be produced during development as a result of:

1. Excessive exposure of the film or plate to light.
2. The use of a safelight which is not suitable for that particular sensitive material.
3. A developing solution incorrectly compounded, containing too much alkali, too little restrainer, used without proper dilution or at a temperature above normal.
4. A developing solution contaminated with hypo or metallic salts such as those of tin, copper or zinc. Traces of these salts may be due to old brass faucets or piping, to developing tanks and equipment of brass, to the use of solder in the construction of the processing equipment, or to mixing developers in galvanized vessels.

5. A developing solution containing sodium sulfide formed by the reduction of the sulfite by bacterial or fungous growths. This occurs ordinarily only in the deep tanks employed in photo finishing or in motion picture production where the developer is used without changing for several weeks. A developer which produces sulfide fog may be reconditioned by the addition of from 0.5 to 0.75 gram of lead acetate per liter. If the developer still fogs, it should be discarded.

Sulfide fog may be prevented by keeping tanks and processing equipment clean and by sterilizing the tanks periodically with a solution of sodium hypochlorite followed by rinsing in water.

6. Excessive exposure of the sensitive material to air during development. The fog produced through oxidation of the developer when the developer-laden film is exposed to air during development is known as aerial or oxidation fog.[1] Under ordinary conditions, aerial fog occurs only with developers containing hydroquinone, but may be produced by other developing agents if contaminated with copper and tin salts. Aerial fog may be prevented by the addition of a small quantity of used developer or a desensitizer. One part of Pinakryptol green to 50,000 parts of developing solution is sufficient to prevent aerial fog under ordinary conditions.

An excess of sulfite will produce what is termed sulfite fog. Silver bromide is soluble in sodium sulfite, and the fog produced by an excess of sulfite is due to the reduction of the silver salt dissolved by the sulfite to metallic silver by the developer.[2] The amount of sulfite required to produce fog varies with different developers but is usually not less than 50 grams of sodium sulfite per liter. Where a large quantity of sulfite is required as in tank developers designed for continuous use or in fine-grain developers, the amount of potassium bromide should be increased, or the developer conditioned by the addition of a small quantity of used solution, to prevent sulfite fog.

Developer or Oxidation Stain.—Stains due to the oxidation of the developer may arise from:

1. The use of an incorrectly prepared developer lacking sufficient sulfite to prevent excessive oxidation.

2. Developing at a temperature above normal thus favoring increased oxidation of the developer.

3. Exposing the sensitive material to air during development, before transferring to the fixing bath, or in the early stages of fixing.

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[1] Crabtree, *American Annual of Photography* (1920) 20.

[2] Mees and Piper, *Phot. J.* **51** (1911) 226; **52** (1912) 221.

4. The use of an old, oxidized developer.

5. The use of a plain fixing bath, or a partially exhausted acid fixing and hardening bath lacking sufficient acid to neutralize the alkali in the developer carried over on the sensitive material and prevent its oxidation.

The use of a stop bath is an almost certain preventative of all stains produced by oxidation after removing the film from the developer.

Developer stains may be removed as follows:

First harden the film by bathing for two or three minutes in an alkaline solution of formalin and wash for five minutes, otherwise the gelatin is apt to soften and frill during the subsequent treatment. Then bleach in:

	Metric	*Avoirdupois*
Stock Solution A		
Potassium permanganate	5.3 gm.	75 gr.
Water to make	1 liter	32 oz.
Stock Solution B		
Sodium chloride (table salt)	75 gm.	2½ oz.
Sulfuric acid (pure concentrated)	16 cc.	½ oz.
Water to make	1 liter	32 oz.
Use equal parts of *A* and *B*.		

The solutions *A* and *B* keep well if kept separately, but not when mixed, and for this reason the bleaching-bath should be prepared as required.

The bleaching should be complete in about three or four minutes when there is usually left a general brown stain all over the film due to manganese oxide, and especially in those parts previously occupied by the image. It is best to remove this stain by first rinsing in water and then placing in a 1% solution of sodium bisulfite. Wash for 3 or 4 minutes, and expose to a strong light (sunlight or arc light) until the white image turns purple. Then develop in a non-staining developer.

Local yellow stains on prints or negatives may be removed by superimposing a deep yellow filter over the negative and making a positive either by contact or in the camera and from this making a new negative. A panchromatic plate must of course be used and the yellow filter must be a contrast and not an orthochromatic filter.

Yellow Stains.—These consist of compounds of silver left in the film after fixing and washing. The presence of unfixed compounds in the film may be due to (*a*) the use of an old and exhausted fixing bath, (*b*) insufficient agitation of the film when transferred to the fixing bath, (*c*) fixing bath prevented from reaching film by another film, contact with side of tank, hanger, air bell, etc.

Yellowish White Opalescence.—This is due to the presence of finely divided, or colloidal, sulfur and arises from the use of a fixing bath (*a*) containing an excess of acid, or a deficiency of sodium sulfite, (*b*) too warm, or (*c*) the use of a plain potassium alum hardening bath after fixing.

The deposit of finely divided sulfur may be removed with a 10% solution of sodium sulfite used at a temperature of 100 to 120 degrees F. (38° to 49° C.). The film must first be hardened in an alkaline formalin hardener.

Silver stain on the gelatin backing of film may be removed with iodine-cyanide reducer (p. 568) applied with a soft brush or wad of absorbent cotton on a stick.

Silver stains on the emulsion side may be removed (*a*) by photographing on panchromatic film through a strong yellow filter (not always successful) or by treatment with a 1% solution of potassium cyanide (a deadly poison). The cyanide will dissolve the image in time, so the film should be removed as soon as any reduction becomes apparent and washed thoroughly before drying.

Silver Stain (Dichroic Fog).—This consists of finely divided silver and is reddish green by reflected light and pinkish by transmitted light, hence the name dichroic (two-colored) fog.

It is due to presence of a silver solvent in the developer, such as hypo, ammonia or sodium sulfide, or developers having an excess of sulfite or alkali, particularly when partially exhausted or when used at high temperature.

It may also be produced in an old fixing bath heavily loaded with silver and partly oxidized developer.

Silver stains can sometimes be removed by reduction in a ½% solution of potassium permanganate until removed, followed by a 5% solution of potassium metabisulfite to remove the brown oxide of manganese stain.

Sulfur Stains (Yellowish White).—Produced as a result of the precipitation of sulfur on the gelatin. Common sources are:

1. A fixing bath which contains too much acid or too little sulfite.
2. A fixing bath which is too warm.

Sulfur stains may be removed by bathing the negative in a 10% solution of sodium sulfite at a temperature of 100° F. (38° C.). The emulsion should be hardened first in an alkaline solution of formalin.

Aluminum Sulfite Stains (Powdery White).—These are due to the use of an incorrectly compounded fixing bath containing insufficient, or impure, sulfite, an excess of acid, or one which is partially exhausted.

A frequent source where none of these factors is present is lack of agitation in the fixing bath.

Such stains may be removed by bathing the film in a 5% solution of sodium carbonate and washing thoroughly. The gelatin should first be hardened in a solution of alkaline formalin.

Stains (Green).—A general green stain is sometimes produced when a hardening bath of chrome alum is used between developing and fixing, particularly if the concentration is too high or the temperature above 80° F. (27° C.). Ordinarily, the only effect is to increase the time of exposure in printing. Usually, the stain can be removed by immersing the negative for a few minutes in a 5% solution of potassium citrate or potassium hydroxide. This treatment should be preceded by an alkaline formalin hardening solution.

Air Bells.—These are small circular transparent spots produced by air bubbles adhering to the emulsion surface and preventing development.

Circular, transparent spots with diffuse edges are produced when the bubble grows smaller as development proceeds.

Spots with a center of lesser density are produced when the air bell breaks or is dislodged.

Spots with unfixed silver halide are due to air bells in fixing.

Clear spots with a dark ring are due to developer oxidation fog around the air bubble.

The presence of a trace of oil or grease is an infrequent cause of air bells. In this event, the negatives should first be immersed in a 2% solution of sodium carbonate, followed by two or three minutes washing in running water before development.

Spots.—Spots having dark narrow outlines are often caused by drops of water remaining on the film during drying.

Hazy white spots appear occasionally on negatives which are dried rapidly at high temperatures particularly when the processing solutions have been warm.

Spots surrounded by gray halos appear at intervals on negatives as a result of drops of water adhering to the base side of the film. When the negative is dried at room temperature, such spots are usually just barely visible, but become more prominent when drying rapidly at a high temperature. Spots of this nature as well as others due to the presence of drops of water during drying may be prevented by the efficient removal of the water on the surfaces of the negative before drying.

Irregular spots, almost clear, are sometimes due to traces of oil or grease on the emulsion or in the developer.

Frilling.—The emulsion softens along the edges and shows a tendency to leave the support; is more likely to occur with double, or thickly coated materials. Caused by the solutions being too warm, a developing solution which is strongly alkaline, a fixing bath which is exhausted or does not harden properly, or processing solutions at different temperatures. There is no remedy.

Reversal.—Image appears partly negative partly positive. Caused by exposure to an unsafe light in development, or a momentary exposure to white light, after development has begun. Sometimes caused by presence of hypo in developer. In this case, the unexposed areas are clear. Reversal by exposure to an unsafe light fogs the unexposed areas.

Streaks on Negatives After Drying with Alcohol.—Impure or exhausted alcohol. Incomplete fixation; alcohol too strong.

Scaly Effects.—Noticeable chiefly in sky or other area of uniform density. Insufficient agitation of developer. A particular type may be due to absorption of water through storage in damp place or exposure to damp air.

Row of Spots Along One Side.—In tray development due to part of film being immersed in one direction and the remainder from another direction. When the two wet areas meet air bells are formed.

Black Spots with Dense Tails.—Undissolved developing agents or alkali.

Yellow or Reddish Patches on the Negative.—Incomplete fixation. Printing from a damp negative on print-out-paper.

Band of Lesser Density Along One Side.—Film not completely immersed in washing tank. Hypo-laden gelatin is reduced by exposure to air.

Dark Line, or Band, Where a Shadow Area Joins a Heavy Density.—Due to the use of a partly exhausted developer and lack of agitation. The developer, not being kept in motion, diffuses from the area where it has had little work to do and produces a higher density along the junction line. Occurs most often in tank development when using dilute developers. Frequently known as the "Mackie" line.

Brown Scum.—This occurs in tank development when solutions are used over a period of time and consists of developer oxidation products which form a scum on the surface of the solution which is picked up by the film when placed in the developing tank.

It may be prevented by skimming the surface of the solution before use with the edge of a piece of blotting paper or cheese cloth on a wooden or wire frame.

Scum marks on developed negatives may be *removed sometimes* with a 1% solution of potassium cyanide.

Fine Black Marks.—These are due either to abrasion or to static discharges arising from friction.

Rough, Whitish Deposit on Negative.—This is due to chalk in the water used in preparing the developing and fixing solutions or in the wash water. It may be removed by placing the negative for several minutes in a dilute solution of ½% hydrochloric acid or in ordinary vinegar, then washing and swabbing the surface thoroughly with a viscose sponge or absorbent cotton.

Traces of the Dye Backing Remain.—The dyes used in non-halation backings are usually discolored by the sulfite of the developer or the fixing bath. Should traces remain after fixing and washing, the negatives should be placed in a 5% solution of sodium sulfite, or in a fresh acid fixing bath, for about five minutes and then washed for five to ten minutes before drying.

Reticulation.—A wrinkling of the gelatin producing a leathery appearance caused by strains produced in the gelatin when it is transferred from one solution to another at a much higher or lower temperature, or from a highly alkaline developer to a strong acid fixing bath. There is no remedy.

CHAPTER XX

REDUCTION AND INTENSIFICATION OF THE NEGATIVE

Photographic Reduction.—The operations by which silver is removed from the photographic image constitute what is properly termed photographic reduction. Photographic reduction, however, is not a process of chemical reduction but of oxidation, and photographic reducers are substances capable of converting metallic silver into a silver compound which is soluble in water, in an acid, or other suitable solvent.

Photographic reducers may be classified as follows:

a. Subtractive: Reducers of this type remove an equal amount of silver from all densities (Fig. 314), thus increasing the density range of the negative. Subtractive reducers are used principally to improve overexposed negatives and positives or for removing fog.

b. Proportional: Reducers of this type remove from each density an amount of silver which is proportional to that of the original density (Fig. 314). Proportional reducers are useful chiefly as a means of reducing excessive density and contrast due to overdevelopment.

c. Super-proportional: With reducers of this type a greater proportionate amount of silver is removed from the higher densities than from the lower (Fig. 314). Super-proportional reducers are used principally for the reduction of overdeveloped negatives of contrasty subjects.

Ferricyanide-Hypo Reducer.—This well-known reducer is frequently termed Farmer's reducer from its originator Howard Farmer.[1] The chemical reaction is as follows:

$$(a)\quad 4Ag + 4K_3Fe(CN)_6 = Ag_4Fe(CN)_6 + 3K_4Fe(CN)_6,$$

$$(b)\quad 3Ag_4Fe(CN)_6 + 16Na_2S_2O_3 = 4Na_5Ag_3(S_2O_3)_4 + 3Na_4Fe(CN)_6.$$

The silver image is oxidized by the ferricyanide, forming silver ferrocyanide which is dissolved by the hypo.

The action is in the main subtractive but depends upon the nature of the silver image and the concentration of the reducing solution. With a relatively strong solution (1 per cent potassium ferricyanide and 10 per cent hypo) subtractive reduction is obtained with both negative and fine-grain positive film but with a dilute solution contrast is decreased and the action is more nearly proportional, particularly with negative materials.[2]

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[1] *Yearbook of Photography* (1884) 59.

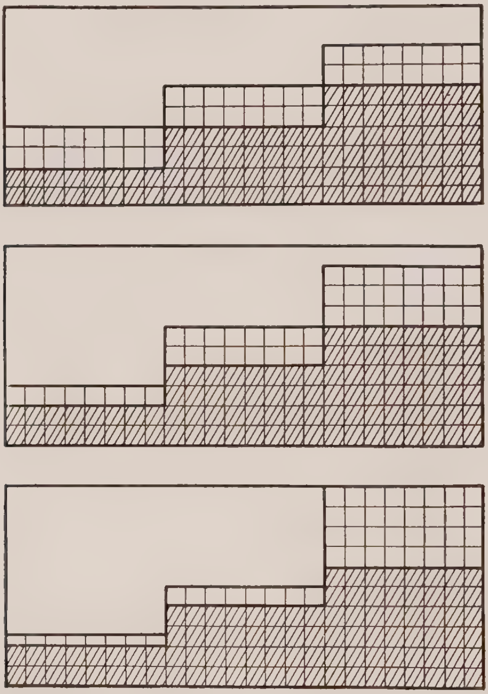

FIG. 314. Diagrams Illustrating Types of Photographic Reduction. (Top) Subtractive, (Center) Proportional, (Below) Super-Proportional.

A mixture of potassium ferricyanide and hypo decomposes rapidly, hence the reducer is kept as two stock solutions:

Stock Solution A		
Potassium ferricyanide (Red Prussiate) .	37.5 gm.	1¼ oz.
Water	500.0 cc.	16 oz.
Stock Solution B		
Hypo	480.0 gm.	16 oz.
Water	2.0 liters	64 oz.

If, after five minutes, further reduction is required, the negative should be transferred to a fresh solution to avoid stain. When the negative has been reduced sufficiently, wash thoroughly. To prevent excessive reduction from the continuing action of the reducer contained within the gelatin layer, the negative upon removal from the reducing solution should be flushed with an abundance of cold water.

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[2] Crabtree and Muehler, *J. Soc. Mot. Pict. Eng.* **17** (1931) 1001.

Almost proportional reduction is obtained with ferricyanide and hypo by treating the negative in the ferricyanide solution first and subsequently in the hypo solution. The degree of reduction depends upon the quantity of silver ferrocyanide formed in the first bath which in turn depends upon (1) the time of immersion and (2) the concentration of the solution.[3]

The following formula is satisfactory:

Solution A		
Potassium ferricyanide	7.5 gm.	¼ oz.
Water to make	1.0 liter	32 oz.
Solution B		
Hypo	200.0 gm.	6¾ oz.
Water to make	1.0 liter	32 oz.

Treat the negative in Solution *A* with uniform agitation for 1 to 4 minutes at 65–70° F. (18–21° C.), depending upon the degree of reduction desired. Then immerse in Solution *B* for 5 minutes and wash thoroughly. The process may be repeated if more reduction is desired. For the reduction of general fog, 1 part of Solution *A* should be diluted with 1 part of water.

Ferricyanide and Ammonium Thiocyanate.—This single solution reducer, which is due to Haddon,[4] is of the subtractive type, but, unlike ferricyanide-hypo, is stable.

The chemical reactions are as follows:

$$(a)\quad 4\mathrm{Ag} + 4\mathrm{K_3Fe(CN)_6} = \mathrm{Ag_4Fe(CN)_6} + 3\mathrm{K_4Fe(CN)_6},$$

$$(b)\quad \mathrm{Ag_4Fe(CN)_6} + (\mathrm{X} + 4)\mathrm{NH_4CNS} = \mathrm{XNH_4CNS.4AgCNS} + (\mathrm{NH_4})4\mathrm{Fe(CN)_6}.$$

The following formula is satisfactory:

Potassium ferricyanide	5 gm.	22 gr.
Ammonium sulfocyanide	10 gm.	44 gr.
Water to make	1000 cc.	10 oz.

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[3] *Loc. cit.*

[4] *Brit. J. Phot.* **39** (1892) 49, 60.

After reduction, wash well in running water. If a white deposit appears on the gelatin surface, dip the negative in hypo for a moment and wash well in running water.

Ferricyanide and Cyanide.—A mixture of ferricyanide and cyanide forms a stable reducer of the subtractive type but with the disadvantages of being highly poisonous and having a softening action on gelatin, thus rendering a preliminary hardening bath of formalin necessary.[5]

The following formula is satisfactory:

Potassium ferricyanide	2.5 gm.	10.5 gr.
Sodium cyanide	2.5 gm.	10.5 gr.
Water to make	1000 cc.	10 oz.

Iodine-Cyanide.—A dilute solution of sodium or potassium cyanide and iodine forms a reducer of an intermediate character, being mainly subtractive but tending towards proportional reduction. It has the disadvantages (1) of being highly toxic and (2) unstable so that it must be prepared immediately before use.

The reaction is as follows:

$$2Ag + I_2 + 4KCN = 2KAg(CN)_2 + 2KI.$$

Potassium cyanide	5 gm.	22 gr.
Iodine (crystal)	1 gm.	4.5 gr.
Water to make	1000 cc.	10 oz.

Iodide-Hypo.—Equally as satisfactory and less poisonous is the following in which cyanide is replaced by hypo.

Potassium iodide	10 g.	75 gr.
Hypo	250 g.	4 oz.
Water to make	1000 cc.	16 oz.

This is non-staining, keeps well, and acts slowly and gradually.

Copper Reducer.—A reducer of the subtractive type which keeps well even after use may be prepared from cupric sulfate and hypo.[6]

Cupric sulfate	30 gm.	½ oz.
Sodium chloride	30 gm.	½ oz.
Water to make	780 cc.	12½ oz.

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[5] The use of potassium cyanide and mercuric chloride has been suggested but offers no real advantages. *Eder's Handbuch*, 1883.

[6] Smith, *Brit. J. Phot.* **63** (1916) 574.

Dissolve and add ammonia until the precipitate first formed is redissolved. The solution is a deep blue.

For use, add an equal quantity of

Hypo	360 gm.	2½ oz.
Water to make	780 cc.	12½ oz.

If the action is too rapid, dilute with an equal quantity of water. Any bluish color remaining in the gelatin after reduction may be removed with a 0.02% solution of sulfuric acid.

Permanganate Reducers.—The permanganates are strong oxidizing substances and if an acid solution of potassium permanganate is applied to a negative the silver is oxidized, forming silver sulfate which is soluble in water.

$$10Ag + 2KMnO_4 + 8H_2SO_4 = 5Ag_2SO_4 + 2MnSO_4 + 8H_2O + K_2SO_4.$$

The following is a suitable formula:

I.	Potassium permanganate	50 gm.	24 gr.
	Water to make	1000 cc.	1 oz.
II.	Sulfuric acid, C.P.	50 cc.	24 min.
	Water to make	1000 cc.	1 oz.

For use take 1 part of *A*, 2 parts of *B*, and 64 parts of water. When sufficiently reduced, immerse in plain hypo solution, fresh acid fixing bath, or 5% solution of sodium bisulfite to remove the brown stain, after which wash well.

The formula as given acts as a subtractive reducer. Solutions containing less acid result in more nearly proportional reduction.[7]

Belitzski's Reducer.—This reducer consists of ferric chloride and hypo. Silver chloride and ferrous chloride are formed and the former converted into soluble salts by the hypo.

As a reducer, it is intermediate in character; the slope of the characteristic curve is lessened, but a greater proportion of silver is removed from the lower densities. It thus partakes of some of the characteristics of both subtractive and proportional reducers.

The following formula of Crabtree and Muehler[8] is much to be preferred to earlier ones:

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[7] Robin, *Sci. et Ind. Phot.* 2 (1931) 24.

[8] *J. Soc. Mot. Pict. Eng.* 17 (1931) 1001.

Ferric chloride	25 gm.	365 gr.
Potassium citrate	75 gm.	2½ oz.
Sodium sulfite	30 gm.	1 oz.
Citric acid	20 gm.	290 gr.
Sodium thiosulfate	200 gm.	6¾ oz.
Water to make	1 liter	32 oz.

Proportional Reducers.—Attention has been called to the fact that approximately proportional reduction results from the use of ferricyanide-hypo in two solutions (p. 567) or permanganate in a neutral or very slightly acid condition (p. 569). Quinone or quinone sulfonates with sulfuric acid form proportional reducers, but the gelatin is stained.[9]

The use of mercuric nitrate with nitric acid has been stated to give proportional reduction, the gelatin is softened, however, and it is sometimes difficult to prevent reticulation.[10]

Proportional reduction may also be obtained with solutions of ferric salts rendered slightly acid by the addition of sulfuric acid.[11]

The reaction is probably as follows:

$$2Ag + Fe_2(SO_4)_3 . (NH_4)_2SO_4 = Ag_2SO_4 + FeSO_4 + FeSO_4 . (NH_4)_2SO_4.$$

The gelatin is stained if exposed to air during reduction, or if the negative has not been thoroughly fixed and washed. Prehardening in formalin is necessary to prevent undue softening of the gelatin.

The following is a suitable formula:[12]

Ferric ammonium sulfate (ferric alum)	15 gm.	2 oz.
Sulfuric acid	10 cc.	1¼ fl. oz.
Water to make	1 liter	1 gal.

Proportional reduction may be obtained through the combination of subtractive and superproportional reducers. A suitable combination consists of potassium permanganate and ammonium persulfate.[13]

The following is a satisfactory formula (Huse and Nietz):

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[9] Lumière and Seyewetz, *Brit. J. Phot.* **57** (1910) 625.

[10] Steigmann, *Phot. Ind.* **19** (1921) 697.

[11] Krauss, *Z. wiss. Phot.* **18** (1919) 192.

[12] Crabtree and Muehler, *J. Soc. Mot. Pict. Eng.* **17** (1931) 1001.

[13] Deck, *Brit. J. Phot.* **63** (1916) 391. Huse and Nietz, *Brit. J. Phot.* **63** (1916) 580.

Solution A				
Potassium permanganate	0.25	gm.	38	gr.
Sulfuric acid (10%)	15	cc.	¼	oz.
Distilled water to make	1000	cc.	35	oz.
Solution B				
Ammonium persulfate	25	gm.	¾	oz.
Distilled water to make	1000	cc.	35	oz.

For use take one part of *A* to three of *B*. Do not mix until immediately before use as the keeping qualities of the combined solutions are very poor. The time of reduction is from one to three minutes and after reduction the negative should be placed in a 1% solution of potassium metabisulfite to remove the stain produced by the manganese salts precipitated in the gelatin.

Super-Proportional Reducers.—The number of reducers which act super proportionally is small; the alkaline persulfates alone are of practical utility although benzoquinone, Erdmann's salt $(CO_2(NH_3)_4 \cdot (NO_2)_8K_2)$, and potassium permanganate with ammonium thiocyanate act in this manner under certain conditions.[14]

The persulfates are powerful oxidizers transforming the silver into silver sulfate which is soluble in the solution. The super-proportional action of the persulfates is due probably to the catalytic effect of the silver ions formed during the reaction between the silver and the persulfate. Since the concentration of these ions increases more rapidly in the higher densities than in the lower the effect is to cause greater reduction of the higher densities.[15]

As reducers the alkaline persulfates are somewhat erratic, sometimes refusing to act at all, and always acting more rapidly as reduction proceeds. To eliminate sources of uncertainty the following precautions should be observed:

1. *Use pure ammonium or potassium persulfate.* Some samples contain a trace of iron, the presence of which even to the extent of 1 part in a million is sufficient to affect the performance of the salt as a photographic reducer.[16]

2. *Use distilled water for preparing solutions of persulfate.* The presence of soluble chlorides, bromides, sulfates, and nitrates in the

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[14] Benzoquinone: Lumière, *Brit. J. Phot.* **57** (1910) 625. Erdmann's salt: *Brit. J. Phot.* **52** (1905) 437, 473. Potassium permanganate: Deck, *Brit. J. Phot.* **63** (1916) 391. Huse and Nietz, *Ibid.* **63** (1916) 580.

[15] Higson, *Phot. J.* **61** (1921) 237. Schuler, *Phot. Rund.* **24** (1910) 113.

[16] Sheppard, *Brit. J. Phot.* **65** (1918) 314.

water used for preparing solutions of the persulfates is one of the most frequent causes of the erratic action of this salt as a reducer.

3. *Avoid the use of stock solutions of persulfate.*

4. *Immediately before use add a small amount of sulfuric acid.* The quantity added controls the rate of reduction. Usually 1–2 cc. per 1000 cc. (20 minims to each 32 oz.) is sufficient.

Persulfate	60 gm.	262 gr.
Sulfuric acid	3 cc.	15 min.
Water to make	1000 cc.	10 oz.

The action should be watched carefully as the rate increases with the degree of reduction and the negative may be reduced further than desired before the action can be stopped. Arrest the action by placing the negative in an acid fixing bath. Fix for about 5 minutes and wash.

A second method of securing super-proportional reduction has been published by W. J. Hickman. The negative is first bleached in an ordinary bleaching bath composed of potassium ferricyanide and potassium bromide as used for sulfide toning of prints. It is then washed for 3 to 4 minutes (not longer) and thoroughly re-developed in an ordinary metol-hydrochinon developer. After a brief rinse in water it is ready for reduction.[17]

For this purpose a weak solution of hypo (1 ounce to 20 ounces of water) is used. Reduction begins almost at once and should be followed carefully. When reduction has proceeded far enough the negative is removed and washed thoroughly in running water.

The theory of the process is that potassium ferricyanide is retained by the higher densities and when the negative is placed in hypo, differential reduction takes place from the formation of Farmer's reducer in those portions of the image in which the ferricyanide has been retained.

Super-Proportional Reduction through Bleaching and Redevelopment.—This process, known as "harmonization,"[18] consists in bleaching the image in an acid solution of potassium bichromate, then redeveloping in any non-staining developer until the desired density and contrast are obtained and fixing. The bleaching solution is the equivalent of the well-known chromium intensifier and the result of the

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[17] *Brit. J. Phot.* **80** (Feb. 3, 1933) 59.

[18] Eder, *Phot. Korr.* **18** (1881) 111.

Lluelleyn—Proportional Reduction with Ferricyanide. Brit. J. Phot. **87** (1940) 432.

process is to intensify the lower densities and reduce the higher since these are only partially developed, the undeveloped silver chloride being removed in the fixing bath.

Potassium bichromate	8.0 gm.	1 oz.
Hydrochloric acid (C.P.)	6.0 cc.	¾ fl. oz.
Potassium bromide	5.0 gm.	290 gr.
Water to make	1.0 liter	1 gal.

After bleaching, the negative is washed thoroughly to remove every trace of bichromate, then placed in the following redeveloper:

Elon	2.0 gm.	115 gr.
Sodium sulfite (desiccated)	10.0 gm.	1 oz. 145 gr.
Sodium carbonate (desiccated)	10.0 gm.	1 oz. 145 gr.
Water to make	1000 cc.	1 gal.

The image redevelops slowly and should be watched carefully. When the proper density and contrast have been obtained, rinse and fix in an acid fixing bath and wash.

Intensification.—Processes of increasing the density and contrast of the developed silver image are known as intensification. The increase in density is accomplished in one of three ways:

1. Through the deposition of additional silver on the image. (Silver intensifiers.)
2. The addition of a metallic compound to the image. (Mercury, chromium, etc.)
3. Through the formation of a colored compound of silver, of another metal, or less frequently of dyes.

Intensification with Silver.—Intensification with silver is accomplished through the use of an acid solution of silver nitrate containing a reducing agent such as metol which results in the silver being precipitated preferentially on the silver deposits of the image. The amount of silver deposited is substantially in proportion to that of the image; hence the increase in density is proportional to the original density and the result is much the same as if the negative had been developed to a higher gamma. As the intensified image consists of silver, it should be as permanent as the original. Unlike many other methods intensification is complete in one solution; therefore, it is easily followed and controlled.

Reduction by Re-Halogenisation. Brit. J. Phot. **81** (1934) 498.

Many different formulas for intensifying with silver are to be found in the literature, but many are unstable and cannot be relied upon in practice. The following formula due to Crabtree and Muehler is an improvement over earlier formulas:

Solution 1		
Silver nitrate, crystals	60.0 gm.	2 oz.
Distilled water to make	1.0 liter	32 oz.
Solution 2		
Sodium sulfite, desiccated	60.0 gm.	2 oz.
Water to make	1.0 liter	32 oz.
Solution 3		
Sodium thiosulfate (hypo)	105.0 gm.	3½ oz.
Water to make	1.0 liter	32 oz.
Solution 4		
Sodium sulfite, desiccated	15.0 gm.	½ oz.
Elon	24.0 gm.	350 gr.
Water to make	3.0 liters	96 oz.

Prepare the intensifier solution for use as follows: Slowly add 1 part of solution No. 2 to 1 part of solution No. 1, shaking or stirring to obtain thorough mixing. The white precipitate which appears is then dissolved by the addition of 1 part of solution No. 3. Allow the resulting solution to stand a few minutes until clear. Then add, with stirring, 3 parts of solution No. 4. The intensifier is then ready for use and the film should be treated immediately. The degree of intensification obtained depends upon the time of treatment which should not exceed 25 minutes. After intensification, immerse the film for 2 minutes with agitation in a plain 30 per cent hypo solution. Then wash thoroughly.

The mixed intensifier solution is stable for approximately 30 minutes at 70° F. (21° C.).

Intensification with Chromium.—Intensification with chromium is effected by bleaching the image in a solution of potassium bichromate and hydrochloric acid or one of chromic acid and sodium chloride (or bromide) and then redeveloping in an ordinary developer.

The precise chemical reactions taking place are not definitely known but are probably as follows:

$$2Ag + K_2Cr_2O_7 + 2HCl = 2AgCl + \text{a reduction product of the bichromate, sometimes assumed to be } CrO_2 \text{ or } Cr_2Cl_2.$$[19]

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[19] Lumière and Seyewetz, *Brit. J. Phot.* **66** (1919) 709. Piper and Carnegie, *Amat. Phot.* **40** (1904) 336, 397, and *Ibid.* **41** (1905) 453, and *Brit. J. Phot.* **53** (1906) 367. Crowther, *Brit. J. Phot.* **66** (1919) 709.

When the bleached image is developed the silver chloride is reduced to metallic silver and the chromium compound remains, thus increasing the density.

The chromium intensifier has a number of advantages:

1. It is reliable.
2. The color of the image is changed but little.
3. The image has a high degree of permanency.
4. If the increase in density obtained with a single treatment is not sufficient, the operation may be repeated. The addition of density becomes less and less with each treatment, however, and generally little is gained from more than two treatments. The color of the image becomes more and more brownish with successive treatments.

A satisfactory formula for the bleaching solution is:

Potassium bichromate	90.0 gm.	3 oz.
Hydrochloric acid, C.P.	64.0 cc.	2 fl. oz.
Water to make	1.0 liter	32 oz.

For use, take 1 part of stock solution to 10 parts of water.

The addition of 5 grams of potassium bromide to each liter (⅔ oz. per gallon) results in more rapid bleaching and greater intensification.

Decreasing the acid content of the bleacher results in a high degree of intensification but the time required for bleaching is increased. Practically little is gained from reducing the amount of acid in the above formula.

Incomplete bleaching results in relatively greater intensification of the lower densities than the higher.

After bleaching wash the negative in running water until every trace of the potassium bichromate has been eliminated. Then redevelop in a non-staining developer such as amidol, paraminophenol, metol, or metol-hydroquinone. Developers containing a high concentration of sodium sulfite should be avoided because of their solvent action on silver halide which may result in reduction of the lower densities. Developers containing a high concentration of sulfite also tend to produce brownish-colored images.

Negatives intensified in chromium may be reduced in dilute solutions of hydrochloric (5%) or sulfuric (2%) acid which remove the addition product responsible for the increased density. Only film which has been hardened in formalin should be so treated or the gelatin may reticulate.

BOUCHER—Study of the Contrast Variation Obtained with the Chromium Intensifier. Amer. Annual of Photography **49** (1935) 59.

Intensification with Mercury.—In intensifying with mercury, the image is first bleached in mercuric chloride or bromide. The reaction which takes place is probably

$$Ag + HgCl_2 = AgCl.HgCl.$$

In the redevelopment process which follows this silver mercurous chloride is reduced, producing a compound of silver and mercury or silver and a compound of silver and mercury, depending upon the nature of the redeveloper.

Bleach the negative completely in:

Potassium bromide	22.5 gm.	¾ oz.
Mercuric chloride	22.5 gm.	¾ oz.
Water to make	1.0 liter	32 oz.

Wash for 5–10 minutes in running water. Redevelop in one of the following:

1. *A non-staining developer, such as amidol, paraminophenol or metol-hydroquinone.* Amidol is prefererable since no alkali is required. Alkaline developers containing sulfite exert a solvent action which results in a lower degree of intensification of the lesser densities; these in fact, under certain conditions, may actually be reduced. Fine-grain developers, containing a large concentration of sodium sulfite, are not suitable. Ferrous sulfate is superior to any of the developers mentioned for this purpose but is now seldom used.[20]

2. *Ammonia.* This is frequently recommended but is not desirable because of its solvent action which may result in the lower densities being weakened rather than intensified.

3. *A 10 per cent solution of sodium sulfite.* This results in slight intensification but is not to be recommended (1) because of its solvent action on the image, (2) because the gain in density is slight and cannot be increased by repeating the process.

4. *A 2 per cent solution of sodium sulfide.* This is a satisfactory method of redeveloping if the gelatin has been hardened in alkaline formalin before bleaching. However, the color of the image is brownish and the density is not increased by repeating the process.

5. *A 10 per cent solution of sodium sulfantimoniate* (Schlippe's salt). This results in approximately proportional intensification and

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[20] Chapman Jones, *Phot. J.* **50** (1910) 238.

is one of the most satisfactory means of redeveloping. It is, however, little used at the present time.

6. *Silver-cyanide.* This forms what is known as Monckhoven's intensifier. It results in a high degree of intensification but the very low densities are reduced. This renders it well suited to the intensification of black and white line work, for which purpose it is principally used. The silver cyanide solution is:

Sodium or potassium cyanide	15 gm.	2 oz.
Silver nitrate	22.5 gm.	3 oz.
Water to make	1 liter	1 gal.

Note: The cyanides are deadly poisons and should be handled with extreme care.

Dissolve the cyanide and the silver nitrate separately and add the first to the second until a permanent precipitate is just produced. Allow the mixture to stand an hour or so and then filter.

Only the images which are redeveloped in ferrous oxalate or in sodium sulfide may be regarded as permanent.

Single Solution Mercury Intensifiers.—

Mercuric thiocyanate	100 gm.	765 gr.
Ammonium sulfocyanide	60 gm.	460 gr.
Potassium thiocyanate	80 gm.	615 gr.
Water to make	1000 cc.	16 oz.

For use dilute 1 part with 10 of water.

Another formula:[21]

Mercuric thiocyanate	200 gm.	1540 gr.
Sodium chloride (salt)	200 gm.	1540 gr.
Water to make	1000 cc.	16 oz.

This also should be diluted with ten volumes of water for use.

After the negative has reached the desired density, it should be washed for 20–30 minutes in running water.

Mercuric-Iodide Intensifier.—This very convenient intensifier is prepared as follows:[22]

Mercuric iodide	2 gm.	90 gr.
Potassium iodide	2 gm.	90 gr.
Hypo	2 gm.	90 gr.
Water to make	100 cc.	10 oz.

[21] Agfa, D.R.P. 109,860; 110,357 of 1899.

[22] W. B. Shaw, *Brit. J. Phot.* **80** (1933) 348.

The ingredients are dissolved together in a little water and the solution made up to the total given. Warm, but not hot, water may be used. The solution may be used repeatedly until exhausted. Intensification is progressive and may be stopped at will, when the density and contrast required have been reached. If only a small degree of intensification is required, the solution may be diluted with an equal quantity of water to make it work more slowly.

While the intensifier contains hypo, it is desirable that negatives be washed for 5–10 minutes before intensification. After intensification, wash in running water for 15–20 minutes. Negatives so intensified are not permanent. To render them completely stable, immerse in a 1% solution of sodium sulfide until the image has been wholly changed —as viewed from the back—from gray to brown-black. The intensifying solution must be kept in the dark or in an amber glass or earthenware bottle.

Miscellaneous Methods of Intensification.—A simple method of obtaining a medium degree of intensification consists in converting the silver image into one of silver sulfide by bleaching and redeveloping in sodium sulfide as in toning prints. Only one degree of intensification is possible, as no increase in density is obtained by repeating the process.

The negative should be hardened in alkaline formalin before bleaching or the gelatin may be unduly softened in the alkaline sulfide bath.

Other toning processes such as those employing the ferrocyanides of uranium and copper may be used for the intensification of negatives. An extremely high degree of intensification is possible with uranium and the process is one of the best for faint images. The intensified image, however, is not permanent, as the silver ferrocyanide is readily decomposed into sodium sulfide. Since intensification with such processes is based upon the toning of the image, considerable experience is required to estimate the degree of intensification as the visual appearance of the image is not a direct measure of its printing density and contrast.

Formulas for intensifying with uranium and copper will be found in Chapter XIV.

Intensification may be effected also by mordanting basic dyes to the image, using any of the well known mordants (p. 658). A dye, or combination of dyes, which is free from color is desirable as the degree of intensification is more readily estimated from the appearance of the image.[23]

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[23] Ives, *Brit. J. Phot.* **68** (1921) 186. Lumière and Seyewetz, *Brit. J. Phot.* **73** (1926) 147.

Sensitometry of Photographic Intensification.—A number of studies have been made (1) of the degree of intensification produced by the different methods and (2) the relation of the added density to the original density, but the most complete are those of Nietz and Huse.[24]

First, however, it is necessary to notice the effect of the color of the image upon the degree of intensification. Since positive materials in general are sensitive only to blue light, any change in the color of the image which increases its absorption of blue light is equivalent, from a photographic standpoint, to an increase in density, and thus the effective photographic density may be quite different from the visual density. The ratio of the visually measured density and the effective photographic density is termed the *color-coefficient.* The greater the difference in the density as measured visually and the effective photographic density, the higher the color-coefficient.

The color coefficients for a number of processes are shown in the following table:[25]

Chromium (1 treatment) (D-72 redeveloper, 1 : 2).	M.P. Pan. Neg.	1.05
Chromium (2 treatments) (D-72 redeveloper, 1 : 2)	M.P. Pan. Neg.	1.19
Mercury (D-16 redeveloper)	M.P. Pan. Neg.	1.01
Silver	M.P. Pan. Neg.	1.00
Chromium (1 treatment) (D-72 redeveloper)	M.P. Positive	1.04
Mercury (Monckhoven's)	M.P. Positive	1.08
Mercury (D-16 redeveloper)	M.P. Positive	0.93
Silver	M.P. Positive	1.00

In Fig. 315 the percentage increase in density is plotted as the ordinate against the original densities as abscissae. A line parallel with the base would thus indicate proportional intensification. No intensifier reaches absolute perfection in this respect, although several approach it closely. The distances of the lines above the base indicate approximately the degree of intensification produced with the corresponding methods of intensification.

Local Intensification and Reduction.—Local reduction or intensification is of great assistance at times in bringing out certain details in the shadows or in reducing the density of an over-dense high-

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[24] Abney, *Phot. J.* **44** (1897) 457. Janko, *B. J. Almanac,* 1898, 899. Bennett, *Phot. J.* **53** (1913) 214. Clerc, *Brit. J. Phot.* **59** (1912) 215. Nietz and Huse, *Phot. J.* **58** (1918) 81; *Brit. J. Phot.* **65** (1918) 179, 191.

[25] Crabtree and Muehler, *J. Soc. Mot. Pict. Eng.* **18** (1931) 1001.

Rupprecht—Intensification of Negatives without Increasing Graininess. Photofreund **18** (1938) 59. (Dye method.)

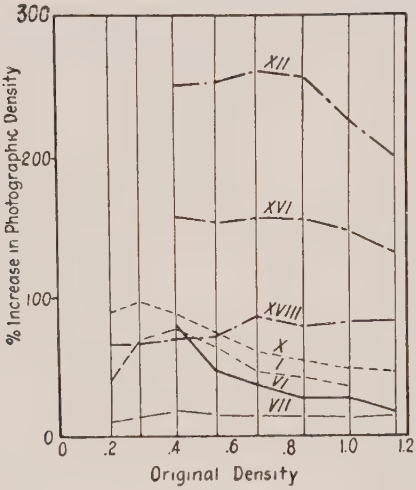

FIG. 315. Illustrating Degree and Character of Intensification Produced by Various Methods. 1. Mercuric Chloride and Ammonia. VI. Chromium and Diaminophenol. VII. Mercuric Bromide and Diaminophenol. X. Mercuric Iodide and Paraminophenol. XII. Uranium. XVI. Mercuric Iodide and Schlippe's Salts. XVIII. Cupric Chloride and Sodium Stannite.

light. Conditions often arise in which local treatment of the negative or "dodging" of some sort in printing is unavoidable. There is often considerable reluctance towards the local manipulation of a negative which may be difficult to replace, and in many cases it is quite true that it is better to reach the desired result through dodges in printing than by work on the negative itself. Still, a little local reduction or intensification, carefully done, is the means of saving a great deal of time and waste of materials in printing.

If the negative to be reduced or intensified has been allowed to dry, it should be first soaked for fifteen to twenty minutes in water, while if the negative has been handled it may be well to add to the water a small amount of sodium carbonate to remove any grease present on the film.

The principal difficulty in local reduction or intensification with the usual methods is to confine the action of the reducer or intensifier to the area in question. With very small areas it is best to work on the dry film, but if the area is of any size this is likely to lead to streaks. On the wet film, difficulty is experienced in the diffusion of the solution over into adjoining areas where it is not wanted. On the whole, the best practice seems to lie in the use of a moist film, i.e., one from which the *surface* moisture has been removed by swabbing with absorbent cotton and the negative left to drain in the drying rack for several minutes.

For local intensification, the mercuric iodide method seems as satisfactory as anything else, since the growth of density can be watched and stopped when it has reached the proper point. For local reduction, Farmer's ferricyanide-hypo is satisfactory, the principal disadvantage being the likelihood of stains. Better in this respect is a reducer of potassium cyanide and potassium ferricyanide.[26]

To prepare this, equal parts of 2% stock solutions of potassium cyanide and potassium ferricyanide are mixed and diluted as required to a strength which enables its action to be controlled.

For small areas, a water-color brush is the most useful tool for applying the reducer or intensifier. For somewhat larger areas a tuft of absorbent cotton saturated with the solution is less likely to result in uneven action. Unless rather strong solutions are in use, and generally that is not advisable, at least until the worker is experienced, the action can be stopped by holding the negative in a flowing stream under the tap.

Another method of local reduction consists in rubbing down the area, using an abrasive paste such as Eastman Reducing Paste or abrasive pencils such as the Eastman Reducing Pencil.

A most useful method of local intensification lies in the application of dyes to the area to be lightened. A yellow-orange dye suitable for this purpose is supplied by dealers as Coccine. The yellow, orange, and red of the more transparent water colors supplied for coloring lantern slides are also suitable. The well diluted colors are best applied to a moist film with a small brush. As soon as the area has been completely covered, remove the surplus color by blotting with clean blotting paper or absorbent cotton. If the degree of coloration does not appear to be sufficient, repeat the application. Successive application of diluted solutions, the surface color being blotted off each time, is much less likely to result in uneven application than the use of a strong color at the out-set. Some little experience is needed to estimate the printing effect of the color, but once this is gained, local manipulation with dyes is a very useful and convenient addition to methods of local control.

The ordinary lithographic pencil, applied to the back of the negative, is often very helpful in holding back small areas which print too dark. The mark is easily removed.

[26] Lighton, *Brit. J. Phot.* **73** (1926) 643.

JAMIESON—Reducing Solution for Local Use (Etchadine). B.P. 461,891.

CHAPTER XXI

AFTER WORK ON THE NEGATIVE

Blocking Out.—The first essential for good work is a good desk. One which is too small is exceedingly trying to the temper and disastrous to good work. There should be a flat smooth surface sufficiently large to allow plenty of elbow room. It is best made of heavy glass and either flat or inclined at a very slight angle. The light beneath should be of good intensity and well diffused. Not all the light from the outside should be stopped out; it is important to be able to see the *surface* of the negative as well as to see through it.

A few good sable brushes of various sizes, a jar or tube of opaque, a drawing pen, a straight edge, preferably of metal, and a celluloid draftsman's curve complete the necessary accessories.

The negative should be clean and free of finger marks. If present, they should be removed with a tuft of cotton wet with benzine or carbon tetrachloride.

Where the subject contains a number of straight lines it is well to rule these with a draftsman's ruling pen, starting with the horizontal lines and ruling all of these first, then the vertical lines. Many of the curves may be ruled in by using the draftsman's curve; those which cannot, must be filled in freehand with a small brush. In using the brush, it is essential, if clean work is to be expected, that the hand should not be cramped. A free, rather flowing motion of the hand from left to right and away from the body, using the fingers underneath the brush as a sliding pivot, leads to smooth, clean work.

When the outline has been completely filled in, the next step is to widen the narrow line which now surrounds the subject. This is done with a somewhat larger brush; then any large areas are filled in with a still larger brush.

When dry, the negative should be given a thorough inspection. Small imperfections can be removed by using a slightly moistened brush, which must be cleaned after each stroke, but if much of such alteration is to be done, something is wrong with the blocking-out technique and the worker needs more practice.

Black Backgrounds.—At times, it is desirable to introduce a black background. There are several methods: The negative may be coated with collodion diluted with an equal part of alcohol and ether. Then the part of the negative to be removed is bleached with a solution of iodine, this part of the operation being analogous to blocking out with opaque. As soon as the area covered is seen to be clear and opalescent on the back, the plate is thoroughly washed under the tap and the negative immersed in hypo which removes the image. Finally, the plate is gone over with a piece of absorbent cotton, saturated with alcohol and ether to remove the collodion, washed and dried.

David Charles, writing in the *British Journal of Photography,* recommends bleaching out the background in a solution of potassium bichromate and hydrochloric acid as used for chromium intensification. The bleaching solution (rather stronger than for intensifying in the ordinary way) is applied with a brush, and when bleaching is complete, the negative (still held flat) is slipped into a 1 per cent solution of sodium carbonate which stops the action of the bleacher immediately. The negative is then washed three or four minutes and examined for rough edges where the background has not been completely removed. These edges are then touched up with the bleacher until the outline is clear and the negative placed again in the carbonate solution. Upon removal from the solution, it is washed one or two minutes, and placed in a plain hypo solution to remove any traces of the image which remain. Finally, it is washed and dried as usual. If any slight errors have been made in bleaching away portions of the image which are to remain, these can be restored before the negative is fixed by applying developer followed by fixing-out when they have attained the proper density.[1]

A second method of introducing a black background is to go over the image to be preserved with a water-proof varnish. When this is dry, immerse the entire negative in any clear working reducer until the background is reduced out. If the negative is thoroughly dry when immersed in the reducer, and the reducing solution is one which acts quickly, there will be no spreading of any consequence under the coated image.

Titles on Negatives.—The title or number may be lettered directly on the back side of a film negative, but unless one is able to letter well this should not be attempted, as poor lettering is a draw-back to any print. Glass negatives must, of course, be lettered in reverse on the film side. So few are sufficiently experienced in this—even expert draftsmen—that it is seldom practical.

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[1] Charles, *Brit. J. Phot.* 79 (1933) 779.

Titles can be printed on negatives with rubber type, using an opaque ink. Sets of reversed type (photoscript) for printing on the emulsion side of the negative are obtainable commercially. Reversed type is not really necessary with film negatives, as the title may be printed on the back side.

Opaque paper letters of a suitable size, ready gummed (Dennison), may be used to number or letter negatives.

There are a number of ways of printing in the name of the studio without much additional trouble. One of the best of these is to letter, or have a printer set up, the desired lettering in type of suitable size and print on a thin transparent celluloid. Have the printer dust over the impression on the celluloid with lampblack before the ink dries. While having the work done, it is well to have several made up, as it is cheaper to have a number made at one time and those not needed immediately can be kept until required. The sheet of celluloid is placed between the negative and the paper when exposing the print so that the lettering appears in the position desired. The sharpness of the print will not be visibly affected as the celluloid is very thin.

Neat, clear-cut titles may be made by placing a sheet of Kodapak or cellophane a trifle larger than the negative between two sheets of black carbon paper with the waxed sides facing the cellophane and typing the desired inscription through a sheet of thin paper. The carbon paper being placed on both sides of the cellophane produces a copy with sufficient density to print white.

To make black letter titles on a white background, make a negative of the copy on process film and double print; print the negative first and then the title. To save film, only the title itself need be photographed, the smaller film being masked so as to protect the rest of the print when printing.

Retouching of Portrait Negatives.—The retouching of portrait negatives is frequently necessary for the removal of skin blemishes, and other imperfections, to improve the modeling and obtain a more pleasing effect. The amount of retouching required may be kept at a minimum by using color sensitive photographic materials, by lighting softly so as to avoid deep and sharply defined shadows, by using a soft-focus lens, diffusion disks, or other devices for softening the definition of the image, and by printing on a matte or rough paper.

The following materials are required:

Retouching desk
Retouching pencils (H, 2H, 3H and 3B)
Bottle of retouching medium
Etching knife
Absorbent cotton

Retouching desks may be purchased (Fig. 316) or built. A piece of opal glass should be fitted flush into a desk supported at an angle of about 40° and a 40 to 60 watt electric lamp placed below to illuminate the negative. If this arrangement is not convenient, the light reflected from a white cardboard may be used.

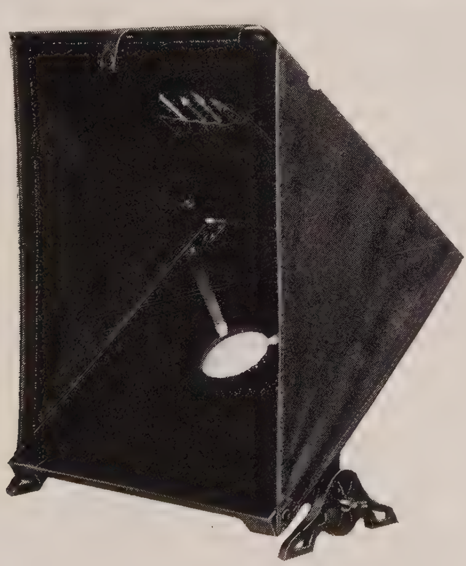

Fig. 316. Retouching Desk.

Retouching pencils are supplied in various grades, or degrees of hardness, designated by the letters H, 2H, 3H and B, meaning black. For the beginner three grades, H, 2H and HB, are recommended. For retouching, the point of the pencil must be needle-sharp. This necessary condition is secured by sharpening the point on a sheet of fine emery paper.

Retouching medium may be purchased or made according to the following formula:[2]

[2] Whiting, *Retouching.*

Pale gum resin	22.5 gm.	200 gr.
Gum dammar	10 gm.	90 gr.
Gum mastic	2.25 gm.	20 gr.
Oil of juniper	6 cc.	1 dram
Oil of turpentine	100–200 cc.	2–4 oz.

The gums are first powdered and then added to the oils; finally sufficient powdered asphaltum is added to give the mixture a dark amber color.

A drop or two of the retouching medium is placed on the part of the negative to be retouched and spread in a thin layer with a soft cloth or absorbent cotton, using a circular motion. Ridges or streaks, especially along the edges, are to be avoided.

The etching knife is used to reduce the density of small areas on the negative by scraping away some of the silver deposit. Success with the etching knife depends in a large measure upon its sharpness: it must be kept as sharp as a first quality razor or it will not be possible to shave away the silver deposit without producing scratches. Any etching required on a negative must be done before applying the retouching medium.

Retouching the Face.—It is essential before proceeding that the beginner have a clear idea of what he is attempting to do.

Retouching is a corrective process and it is not necessary to apply lead to the whole of the face but only where skin blemishes or other imperfections have resulted in a lower density than the surrounding portions. Beginning with the highlights, take one such spot and work on it until it disappears. Various strokes are used by retouchers in removing spots and suggesting skin texture. In the beginning, however, one should not pay so much attention to the stroke as to filling the spot with fine lines so that at a distance of ten or twelve inches it matches the density of the surrounding portions and is no longer perceptible. Do not attempt to fill up the spot solidly, or at once, but use a relatively hard pencil, such as 3H, and work slowly and patiently, filling each spot with a network of fine crosslines.

Begin in the highlights and work towards the shadows, using a more delicate touch in the shadows or thin portions of the negative than in the higher densities.

Modelling.—When the spots due to freckles and other skin blemishes have been removed, the beginner would do well to make a print to see the effect of his work. If it is unsatisfactory, he can remove the results of his labors by rubbing with a soft cloth containing retouching medium. It is probable that an examination of the negative will show certain areas to be blotchy, and gradations of tone which are abrupt or ragged. Perhaps there are some shadows which need to be lightened or highlights which must be blended with the surounding areas. This may be undertaken next, using a fine, light stroke and a relatively hard lead. A knowledge of anatomy is a great asset at this stage. One must be careful to retain the character of the subject and avoid work which will show in the print. Retouching which attracts attention is often worse than none at all.

Retouching Individual Features.—Because of the method of lighting the subject, wrinkles and other character lines sometimes appear unduly prominent, and need to be subdued. They should not be removed entirely, especially in the case of men or old people. It is often well to idealize women's portraits, however, but not to the extent of destroying individuality.

Care must be taken to preserve the real character lines and merely soften unpleasant features. For instance, the transverse furrows in the forehead may be exaggerated, especially in the case of older people. These can be toned down but the two highlights on the upper part of the forehead and the two above the eyes should be preserved.

When retouching the nose, begin on a line with a corner of the eye and work down the length of the bridge, blending softly down the side. If the shadow at the side of the nose is filled in too heavy, the nose will appear to blend into the cheek.

Work on the cheek should begin on the highest light, and extend back to the side and down about half way to the shadow between the neck and the chin. If carried on down, the chin may be made to appear too large. Sunken cheeks may have the shadows filled in somewhat.

But little work is needed on the chin and this should emphasize the highest light. Never work from the chin clear to the lips, or the shadow between the lips and chin may be lost.

Breaks or imperfections on the lips should be carefully filled, using light straight strokes.

Any lines at the corners of the mouth having a downward tendency may be softened somewhat.

The eye is the seat of expression and any attempt to modify it must be very carefully done. The catch light should ordinarily be on the iris about half way between the top and center of the eye. If it is too large or if it extends out over the pupil, a part may be removed with the etching knife as explained. It is sometimes well to strengthen the iris somewhat but this will make it print lighter in color. The "crow's-feet" and other lines at the corners of the eyes may be softened by partly filling up the shadows.

If enough lead will not adhere to properly build up certain parts, then the negative, if on portrait film, may be turned over and additional work done on the back.[3]

Varnishing.—Two formulas for negative varnish follow:

I	20% shellac solution	160 cc.	2 oz.
	Ammonia (0.880)	30 cc.	3 dr.
	Methylated spirit (methyl alcohol)	320 cc.	4 oz.
II	Japanese gold size		1 part
	Benzole		2 parts

The second is a rather slow drying varnish which, however, takes the pencil well.[4]

It is well to heat the negative slightly before varnishing to eliminate any moisture which may have been absorbed by the gelatin film. If either of the above or other cold varnish is used, the negative should be allowed to cool before varnishing. Film negatives are best treated by drawing them through the solution and then hanging up by one corner to dry. In varnishing glass plates the plate should be held by one corner in a horizontal position and the varnish poured on the center so as to form a pool. Allow this to spread and incline the plate slightly to each corner in succession, allowing any surplus to drain from the last corner into the bottle. If this is done carefully the varnish will not go beyond the edge of the plate. It is well to practice this technique on several waste negatives until it can be done without getting any of the varnish on the back. Allow plenty of time for the negative to dry. Varnishes differ in the amount of time required in drying; heat should not be used, however, to hasten drying.

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[3] *Retouching and Improving Negatives,* Photo-Miniature No. 171, Tennant and Ward (out-of-print but available second-hand). *Retouching Not Difficult,* edited by F. R. Fraprie, American Photographic Publishing Co., 353 Newbury St., Boston, Mass. *Retouching and the Finishing of Photographs,* by J. Spencer Adamson, Frank V. Chambers Publishing Co., 636 South Franklin Square, Philadelphia, Pa. *The Art of Retouching Negatives and Finishing and Coloring Photographs,* by Robert Johnson, American Photographic Publishing Co., 353 Newbury St., Boston, Mass.

[4] *B. J. Almanac* (1936) 353, 354.

Stripping Negatives.—To remove the emulsion from a *glass* negative for transfer to a new support, prepare the following solution:

Wood alcohol	25 parts
Water	1 part
Glycerine	1 part

A sheet of waxed paper slightly larger than the negative, some blotting paper, and a small quantity of hydrofluoric acid will be required.

Place the negative on the back of a tray or on a sheet of glass which is perfectly level. To each ounce (30 cc.) of the above solution, add 10 to 200 drops (1–10 cc.) of hydrofluoric acid and pour over the negative until the surface is covered. Spread the solution, if desired, with the edge of a piece of cardboard. After one or two minutes, try one corner of the film with the fingernail. If free, pull away the edges. When the emulsion appears to be free of the support, apply a sufficient amount of the alcohol-glycerine mixture to cover the emulsion and apply the sheet of waxed paper. Squeegee the paper to the emulsion, using a flat squeegee lightly, and remove the film from the glass by lifting one corner with a penknife and stripping the waxed paper from the glass.

The paper with its adhering emulsion is now placed on a glass plate which has been coated previously with a layer of soft gelatin, squeegeed lightly and the paper stripped, the point of a knife being used to hold the corner of the film on the glass.

The following solution should be used to remove the image from film negatives:

Caustic soda	23 gm.	100 gr.
Formaline	21 cc.	100 min.
Water to	1000 cc.	10 oz.

The negative is placed in this solution until the emulsion layer is loosened, stripped carefully and placed in:

Hydrochloric acid	5 cc.	25 min.
Glycerine	5 cc.	25 min.
Water to	100 cc.	1 oz.

It is then transferred to the new support.[5]

[5] These methods are taken from the *British Journal Photographic Almanac*, 1937.

Morris—The Sterry Stripping Process in Practice. Brit. J. Phot. **81** (1934) 409.

Working-in Backgrounds on the Negative.—Many portrait photographers are quite adept at working-in or altering backgrounds on the negative. The picture, in this case, is made with a black background, the object being to have the background portion clear and free from any detail whatsoever. The negative is then attached to a sheet of ground glass, or to matt celluloid, and the design worked in with lamp black, lead, or charcoal, using a paper stump and a rubber eraser.[6]

Retouching with Dyes.—A most useful method of increasing the density of any portion of the image which may require it, lies in the application of dyes to the area to be lighted. A yellow-orange dye known as neo-coccine, the yellow, orange and red of the more transparent water colors employed for the coloring of prints and lantern slides may be used. Naphthalene black [7] also may be used and has the advantage of being a neutral black, thus enabling the added density to be estimated more accurately. The well diluted dyes are best applied to the dry negative with a small water color brush. As soon as the area to which the dye has been applied has been completely covered, the surplus dye is removed by blotting with clean lintless blotting paper. With the brush in one hand and the blotter in the other, apply successive washes of the dye, blotting each off a moment later until the desired result has been produced. Should too much of the dye be applied, it can be removed by soaking the negative in water. In the case of neo-coccine, it may be necessary in some cases to soak the negative for a few minutes in a weak solution of sodium sulfite or carbonate. Cartwright, writing in the *Penrose Annual* for 1935, suggests that in the case of neo-coccine, the effect of the dye be determined by examining it through a blue-green filter which causes it to appear more or less neutral gray. Berry recommends [8] the addition of precipitated chalk to the solution of neo-coccine to the consistency of a moderately thick cream, which should be applied to the *dry* negative by rubbing lightly, but rapidly with a camel's hair brush or the ball of the finger in the case of larger areas for 10 to 15 seconds and then remove with a soft cloth.

Removing Gelatin Backing of Film Negatives.—Frequently, the gelatin backing of a negative is scratched either in processing or by the handling it receives. Varnishing will usually eliminate scratches if not too deep in which case the gelatin backing must be removed. This may be accomplished[9] by squeegeeing the emulsion side of the negative to glass or Kodaloid, using rubber cement which should first be thinned to the consistency of light molasses with benzole. The addition of 5% by volume of amyl acetate results in better adhesion if Kodaloid or film base is used. The rubber cement, thus modified, is applied to the glass plate, or sheet of film base, and allowed to dry for about 30 minutes, after which the emulsion side of the negative placed on the tacky surface and squeegeed tightly in place. The negative with its glass or film base backing is then placed in 5% sulfuric acid at a temperature of from 100° to 110° F. (38° to 43° C.). The gelatin backing of the negative will become soft in about 15 minutes and may be rubbed off with the tips of the fingers.

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[6] Photo Miniature No. 126, "Putting Backgrounds in Portrait Negatives," or Johnson's "The Art of Retouching Photographic Negatives."

[7] Wakefield, *Brit. J. Phot. Almanac* (1940) 177.

[8] *Camera* (Phila.) (1940) 45.

After the gelatin backing has been removed, the negative is washed a few minutes in running water and stripped from the glass plate or film base. Any rubber cement adhering to the emulsion can be removed easily by rubbing with the finger tips.

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[9] Ross and Crabtree, *Brit. J. Phot.* **73** (1936) 569.

CHAPTER XXII

DEVELOPING PAPERS

Developing Papers.—The emulsions employed for developing papers differ from those employed for negative materials principally in the lower concentration of the reactants used in making the emulsion, resulting in lower dispersity (finer grain) and in containing less silver, per unit area.[1] The amount of silver per 100 square centimeters is given by Sheppard as being of the order of 0.018 grain as compared with 0.10 grain per 100 square centimeters of the average negative emulsion. According to the same authority [2] the grains of silver halide in a developing paper seldom exceed 0.01 to 0.02 micron and are mostly below the resolving power of the microscope.

In general, emulsions for developing papers are not washed to remove the extraneous salts, nor digested or ripened, except for the cold ripening which may take place in storage before or after coating. Various substances, the nature of which is largely a commercial secret, are added to paper emulsions, these additions being necessitated by the properties of the paper base or to control the color of the image.

Papers in which the sensitive halide is silver chloride develop rapidly and are used for both contact and projection printing.

Bromide papers in which the sensitive halide is silver bromide develop slowly producing a black image and are used almost exclusively for projection printing.

Chloro-bromide papers contain both silver chloride and silver bromide and are used for both contact and projection printing. The

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[1] *Photography as a Scientific Implement,* p. 162.

[2] *J. Chem. Ed.* **4** (1927) 298, 465, 749.

Schwarz—Substances Affording Development of Bluish-Toned Images on Gelatino-Silver Chloride Papers. Sci. et Ind. Phot. II **7** (1936) 113.

Seyewetz—Constitution of Substances Giving Bluish Images with Silver Chloride. Proc. Ninth Int. Cong. of Phot. Paris, 1935, p. 360; Sci. et Ind. Phot. II **6** (1935) 300.

Steigmann—Developer and Emulsion Additions. Phot. Ind. **37** (1939) 774, 800.

Steigmann—Green and Brown Developing Emulsions. Phot. Ind. **34** (1936) 764, 872.

speed and image color of these papers vary with the proportions of one halide to the other. In the faster papers producing black images, silver bromide dominates, while in the slower papers designed to produce warm black or brown black images, there is a larger proportion of silver chloride.

Paper Base.—This is always made especially for photographic purposes. It must be free from all foreign substances which would affect the emulsion, cause discoloration of the paper stock with time, and must have the physical strength to withstand the action of the various processing solutions. While pure rag paper stocks were formerly regarded as absolutely necessary for photographic purposes, paper base made from wood pulp is now used and is, in some respects, superior to the rag stocks formerly employed.

Paper stocks for photographic papers differ in three particulars: (1) in *weight* or thickness, (2) *surface* and (3) *color.*

Depending upon the thickness of the base, photographic papers are usually classified as (1) light weight, (2) single weight, (3) medium weight and (4) double weight. Single weight paper is ordinarily used for small prints or for prints to be mounted to solid mounts. Double weight papers are preferred for those left unmounted or if not to be mounted solidly. Light weight papers are used where weight is a consideration and more particularly when a high degree of flexibility is required.

In most cases, a paper is obtainable in several surfaces, the more common being: (1) glossy, (2) semi-matt, sometimes called "velvet," (3) matt, (4) rough, and occasionally (5) very rough. All other surfaces may be regarded as variations of these. The semi-matt, matt and rough papers may or may not have a "sheen" or lustre.

The usual colors are (1) white, (2) natural or cream white, (3) buff, also known as old ivory, and (4) pensé or pink. Blue, green and other paper stocks have been supplied for special effects.

Papers are coated in rolls in much the same way as film, i.e., the paper base is drawn around a roller which dips into a trough containing the fluid emulsion, from which it is conducted in festoons by means of roller conveyors into a chilling room where the emulsion "'sets" and then to the drying room, where the emulsion layer is dried under

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WANDELT—Modern Developing Papers, Phot. Ind. **32** (1934) 1350; Sci. et Ind. Phot. II **6** (1935), 121.

CHARRIOU AND VALETTE—Photographic Emulsions for Printing Papers. Chemie et Ind. **36** (1936) 888.

carefully controlled conditions. Papers with a glossy surface and other surfaces having a tendency to show friction markings are usually supercoated with a layer of plain gelatin by a second coating roller before being conveyed to the chill room.

Variations in the Shape of the *D* Log *E* Curve with the Type of Emulsion.—With papers, as with negative materials, the shape of the *D* log *E* curve varies with the time of development. With chloride and chlorobromide papers in which the bromide predominates, a stable curve shape is reached very quickly, more slowly in the case of warm-tone chlorobromide papers and still more slowly with most bromide papers. Once a stable curve shape is reached, the effect of continued development is to cause the curve to shift laterally to the left.

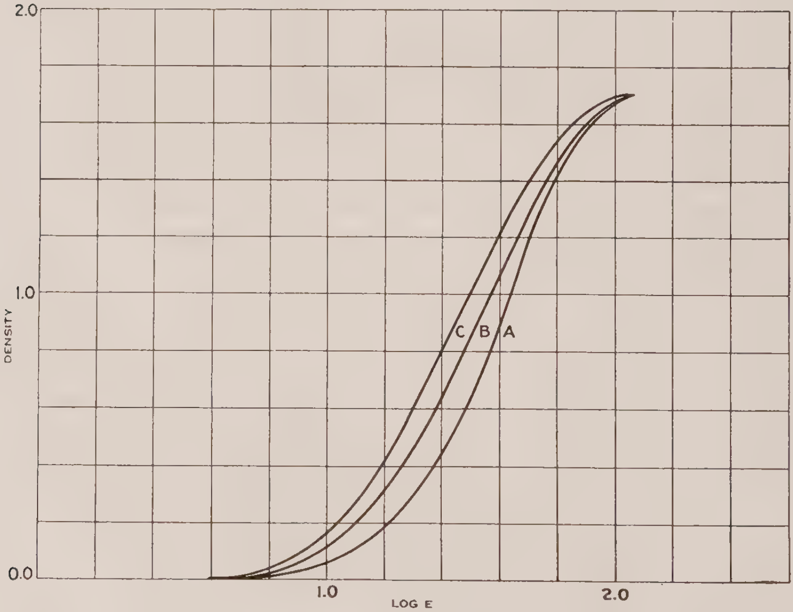

FIG. 317. *D* log *E* Curves of Papers of (*A*) Silver Chloride, (*B*) Silver Chloro-bromide, and (*C*) Silver Bromide, having Approximately the Same Maximum Density and Exposure Scale.

The differences in the shape of the *D* log *E* curves of chloride, chlorobromide and bromide papers are shown in Fig. 317,[3] in which *A* represents a chloride paper, *B* a chlorobromide paper and *C* a bromide paper, all having practically the same contrast and maximum density. It will be noted that the curve of the chloride paper shows little, if any, straight line portion and that the portion most nearly approaching a straight line is in the upper density range. The shoulder portion of the curve is very short. On the other hand, the toe portion is long and sweeping. Curve *C*, representing a typical bromide paper, shows a more clearly defined straight line portion, a more gradual shoulder and a steeper and less sweeping tone portion. Curve *B* representing a chlorobromide emulsion, is of intermediate character, as would be expected. In general, the curve shape of a chlorobromide paper depends upon the relative amount of silver chloride and silver bromide in the emulsion. If the former predominates, the curve approaches that of a chloride paper, if the proportion of bromide exceeds that of silver chloride, the curve takes on the character of a bromide paper.

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[3] Jones and Morrison, *J. Franklin Inst.* **228** (1939) 445, 605, 755.

Variable Contrast Papers.—Within the past year, developing papers in which the contrast of the image may be varied over a wide range by changes in the color of the exposing light, have been introduced commercially in both England and America. With these papers,

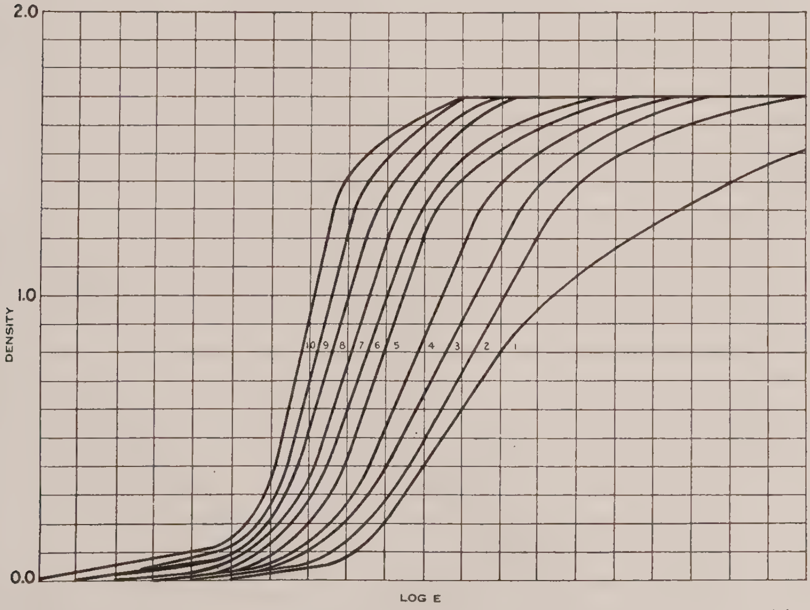

Fig. 318. *D* log *E* Curves of Varigam Paper Produced by Exposing with Different Filters.

it is possible by the use of filters to duplicate, on one paper, the range of contrast obtained on the different contrast grades of other papers. In one of these (Multigrade), two separate emulsion coatings are employed; one of low contrast sensitive only to blue and violet light, the other of high contrast sensitive to green as well as to blue and violet light. Consequently, if an exposure is made with a blue-violet filter, a print of low contrast is obtained. The use of a yellow (minus blue) filter results in a print of high contrast because only the green sensitive emulsion is affected. If an exposure is made first through one filter and then the other, an intermediate degree of contrast is obtained, depending upon the ratio of the two exposures.

The second of the two papers to be introduced utilizes an emulsion in which the gamma varies with the wavelength of the exposing light, hence the name Varigam (varying gamma).

A series of *D* log *E* curves showing the variation in gamma and exposure scale produced with a set of filters supplied for use with the paper is shown in Fig. 318.

Choice of Paper Surface and Color.—The selection of a particular surface and color is to a large measure a matter of personal preference; however, the use to be made of the print is, at times, an important factor. Glossy papers, for example, are preferred for prints for reproduction or where fine detail and a brilliant image is required. Semi-matt papers are used where the glossy surface is not regarded as desirable, but a surface with a decided texture, which would interfere with the reproduction of fine detail, would be objectionable. Matt, or fine grain papers, result in a softer, less brilliant, image which is regarded by many as more "artistic." Rough papers are used chiefly for large prints where the general effect desired is one of breadth, with broad masses rather than detail. This is true to an even greater degree of such extra rough surfaces as tapestry, art canvas, tiger tongue, etc.

The selection as to color depends upon the subject, the color of the image and the effect desired. In general, for subjects with cold colors for reproduction, a white paper stock is preferred. For pictorial work, sunshine effects, portraits, landscapes with foliage, the greater warmth of a cream white, or "natural" color base may be preferable. Buff

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Potter—Varigam—A New Printing Paper. Phot.Tech. **2** (1940) 59.
Renwick—Multigrade—A New Printing Paper. Phot. J. **80** (1940) 320.
Weiland—Bromide Paper Characteristics. Amer. Phot. **34** (1940) 1.

colored paper stock is preferred by many for toned prints, for portraiture, and other subjects for which a warm, colored image is suitable.

Selection of the Proper Grade of Paper.—The proper grade of paper for a given negative depends upon (1) the density range of the negative, (2) the exposure range of the paper, and (3) the requirements for good tone reproduction.

It is evident that if the density range of the negative is too great, the range of exposures produced by the negative will be greater than the capacity of the paper to reproduce, i.e., the negative transmission range exceeds the exposure scale of the paper, and some of the density diffrences of the negative will not be reproduced as tone differences in the print.

If the transmission range of the negative is less than the exposure scale of the negative, only a portion of the available brightness range is utilized with the result that the scale of tones is less than that required for a satisfactory reproduction of the subject.

It is often assumed that the total exposure scale of the paper and the transmission range of the negative should be approximately the same. In this case, the maximum density of the negative is represented by the threshold density of the paper and the minimum negative density by the maximum black of the paper. A careful study of the subject, however, has shown that in practice this procedure is not followed. Occasionally, the maximum black of the paper may be required and on other occasions, the maximum white. In some cases, both are required. The range of exposure between the limiting gradients on the upper and lower portions of the D log E curve is, in general, a more reliable indication of the transmission range of the negative, which will make a good print. These limiting gradients, however, have not been accurately determined. They undoubtedly have some relation to the average gradient of the D log E curve as has been found to be true of negative materials. Moreover, there are undoubtedly many cases in practice in which a particular printing paper is chosen because of the tone separation which it produces, from a given negative, in a particular tone range. In other words, a particular paper may be selected because it produces the desired print density differences *in that portion of the image which is of chief interest;* as for example, the face in a portrait.

For the present, it may be said that the choice of the grade of paper for a particular negative is largely a matter of judgment based upon experience and upon the effect desired and the problems of tone reproduction involved are not now readily expressed in sensitometric terms.

Determining Printing Exposures.—The exposure required in printing depends upon four factors: (1) the intensity of the illumination on the negative, (2) the negative densities involved, (3) the speed of the paper and (4) the effect desired.

Frequently, two interrelated problems are involved in the determination of the exposure: (1) the selection of the proper grade of paper for the negative and (2) the exposure required to produce the desired effect with the paper selected. Information on both of these is ordinarily obtained by means of test exposures which, for the sake of economy, are usually made on strips of paper.

In recent years, the determination of printing exposures from photometric measurements of the negative, or the projected image, has received considerable attention, and a number of devices for rapidly and conveniently making such measurements and determining the exposure have been placed upon the market. In some of these instruments, photoelectric cells are employed, but the majority are visual spot photometers in which the illumination of a selected portion of the image, received on a white field within the instrument, is measured by comparison with the illumination on a small spot being illuminated by a small electric lamp, the intensity of which is varied by means of a rheostat. In some cases, the user is directed to measure the lowest image brightness (highlight negative density), in other cases, the highest image brightness (i.e., the negative shadow density) and in still other cases, the mean of these two values.

The question as to what part of the image affords the most reliable indication of the best exposure has received considerable study.[4] Tuttle, after a lengthy series of investigations in which studies were made of the reliability of the maximum (highlight) negative density, the minimum (shadow) negative density and the total (integrated) density, concluded that "The total density is the best of the three objective criteria of printing exposure—minimum density the second best, while the maximum density is almost valueless."

The latitude, or tolerance, in exposure is less with papers than with negative materials and, for prints of good quality, the exposure must be approximately correct. An examination of the effect of the time of development on the D log E curves of papers (Fig. 255) shows that with chloride papers in particular and with chloro-bromide and bromide papers to a lesser degree, the maximum black of the paper and the final or stabilized curve shape are reached after a relatively short time of development, and that the effect of continuing development is to shift the *D* log *E* curve laterally to the left; i.e., the exposure required for a given print density becomes less as the time of development increases until fog appears or development reaches finality. As applied to papers, latitude in exposure may be defined as the range of exposure over which the average density, of "depth," of the print may be controlled by varying the developing time without producing degraded or unsatisfactory tones.

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[4] Dunn, *Brit. J. Phot.* **84** (1937) 37. Southworth, *Brit. J. Phot.* **82** (1935) 371; **83** (1936) 641. Tuttle, *J. Franklin Inst.* (1937) 315. Tuttle, *J. Soc. Mot. Pict. Eng.* **18** (1932) 172.

Developers and Development.—The development of prints is not essentially different from that of negative materials but certain factors which are relatively unimportant in negative development become of considerable consequence in the development of emulsions on paper. The factors of diffusion and absorption of the developing solution by the gelatin film become much less important, while development takes on more of the character of the so-called "physical" development, i.e., the reduction of the silver from a solution which interacts with the developer. This alteration in the character of development is not due, however, to the use of an accessory solution depositing silver, as in actual physical development, but to the solvent action of the sodium sulfite of the developer on the fine-grained silver bromide and silver chloride.

A factor of major importance in the development of prints is the color of the image. Excluding the effect of the paper base, the color of the image depends upon the dispersity of the silver deposit, i.e., the

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Bierman—Development of Chloro-Bromide Papers. Phot. J. **67** (1927) 444.

Bierman—The Control of Gradation in Bromide Printing by Development. Phot. J. **68** (1928) 456.

Formstecher—Two-Bath Development of Prints on Paper. Phot. Ind. **28** (1930) 551; Sci. et Ind. Phot. (II) **I** (1930) 253.

Jones—The Relationship between the Size of Particle and Color of Image. Phot. J. **51** (1911) 159; Phot. J. **57** (1917) 158, correction of first paper.

Schwarz—Substances Affording Development of Bluish-Toned Images on Gelatino-Silver Chloride Papers. Sci. et Ind. Phot. (II) **7** (1936) 113.

Seyewetz—Constitution of Substances Giving Bluish Images with Silver Chloride. Proc. Ninth Int. Congress of Phot. Paris, 1935. Sci. et Ind. Phot. (II) **6** (1935), 300.

Steigmann—Blue-Black Development. Camera (Luzern), **13** (1934) 100.

average size of the particles of metallic silver comprising the image.[5] The smaller the average particle size, the warmer the color.

With any given paper, the average size of the silver particles and the color of the image depend upon: (1) the composition of the developer and (2) the time of development. The purest black which the paper will yield is obtained when the solvent effect of the developer is at a minimum, i.e., when a relatively large proportion of alkali is employed with only sufficient restrainer to prevent fog and when the image is developed to finality, i.e., until the latent image is completely developed.

For bromide and chloride papers which are designed to produce prints with a black or bluish black color, metol-hydroquinone developers have almost completely displaced all others, although diaminophenol is preferred by some workers.[6, 7]

To obtain warm tones on chloride or chloro-bromide papers, the alkali is reduced and the amount of bromide or other restrainer increased in order (1) to increase the solvent action of the developer and (2) to prevent the complete development of the exposed grains of silver halide before an image of satisfactory gradation and quality is obtained. The use of developing agents of low potential, such as chloroquinol and glycin, alone or in combination with metol and hydroquinone, is favorable towards the production of warm-colored images because of their greater sensitivity to the restraining effect of potassium bromide. Increasing the amount of restrainer tends to produce warmer colors due to the increased solvent action of the developer, while reducing the time of development and increasing the exposure accordingly also tend to produce warmer tones.

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[5] Jones, *Phot. J.* **51** (1911) 151.

[6] The production of blue-black tones is facilitated with many papers, particularly those of the slow silver chloride type, by the addition to the developer of nitrobenzimidazol, benzotriazol, nitroimdazol, nitrosoquanidine, thiosemicarbazide, thiosemicarbazone, thioglycollic acid, 5-amidoquanide, quinone chloride, iodosobenzine, quinoline and potassium sulfocyanate.

Steigmann, *Phot. Korr.* **68** (1932) 75; *Sci. et Ind. Phot.* **7** (1936) 74; Steigmann, *Camera* (Luzern) **13** (1934) 100; *Sci. et Ind. Phot.* **6** (1935) 299; Seyewetz, *Sci. et Ind. Phot.* **6** (1935) 300; Kieser, *Phot. Ind.* **31** (1933) 997; Gossler, *Phot. Ind.* **32** (1934) 476, 782; (1936) 1127; I. G. Farbenindustrie, *Phot. Ind.* **33** (1935) 502; *Brit. J. Phot.* **83** (1936) 552.

[7] A very important factor in the production of good black tones is the use of a fresh developer. Chloride papers are very sensitive to soluble bromide, and, since the amount of bromide in the developer increases with every print developed, it is obvious that the developer must be renewed frequently if constantly good print quality is to be obtained. Contamination of the developer with hypo or other substances having a solvent effect on the silver halide is likewise to be avoided. Very small traces of hypo have a marked effect on the color of the image, changing it from a good black or blue-black to a degraded color.

The Development of Prints.—Since prints are invariably developed by inspection, an abundance of light, provided it is safe for the paper in use, is a decided convenience. In general, printing papers are sensitive only to ultraviolet, and blue and violet light, so that a yellow safelight provides adequate safety with good visibility. Some papers, however, are sensitive to yellow and still others to light orange. In any case, the recommendations of the manufacturer should be followed in this, as in other, respects. Tests of the safety of the illumination in the printing room may be made by exposing a sheet of paper, partially covered, for about 30 seconds, and developing *in darkness* for the usual time. If the light is not safe, the exposed portion of the paper will show a slight veiling.

All papers, and in particular chloride papers for contact printing, which develop rapidly, must be quickly and evenly immersed in the developing solution to avoid uneven development of the image. The print, with the emulsion side up, may be slipped beneath the surface of the developer with a quick motion of the hand, or with the emulsion side down, the print may be covered in a continuous sweep by drawing it, by one corner, through the solution.

Papers are very susceptible to stain and to avoid staining from the oxidation of the developing solution, prints should be exposed to air during development as little as possible. Since the rate of oxidation and the rapidity of development increase with the temperature of the developing solution, the temperature should not exceed 70° F. (21° C.) if at all possible. Cold developers, owing to the lower energy, lead to over-exposure and prints of poor color because of underdevelopment.

Considerable experience is required with a paper in order to be able to judge the progress of development, since the appearance of the image in the developer varies with the paper and to some extent with the surface. In general, the image as seen by the safelight appears of higher average density, lower contrast and with less density or "depth" in the shadows than after fixing. Fixing makes the image appear more brilliant by removing silver halide which being yellow colored has the effect of making the highlights appear slightly darker and the shadows lighter under the safelight.

VARDEN—Two-Tray Development. Phot. Tech. **2** (1940) Oct. p. 32.

Control of Contrast Through Modification of the Developer.—The contrast of the print may be determined to some extent by modification of the developer. In a metol-hydroquinone developer, increasing the metol and decreasing the hydroquinone and alkali will tend to decrease contrast, while increasing the amount of hydroquinone and alkali increases contrast. The laboratories of Agfa-Ansco have found that the addition of glycin tends to increase the contrast still further and recommends two formulas:[8]

	Agfa No. 120 For soft prints		*Agfa No. 130 For contrast prints*	
Hot water (125° F. 52° C.)	750 cc.	24 oz.	750 cc.	24 oz.
Metol	12.3 gm.	¼ oz. 70 gr.	2.2 gm.	32 gr.
Sodium sulfite (des.)	36.0 gm.	1 oz. 88 gr.	50 gm.	1¾ oz.
Sodium carbonate (des.)	36.0 gm.	1 oz. 88 gr.	78 gm.	2½ oz.
Hydroquinone	——	——	11 gm.	¼ oz. 50 gr.
Potassium bromide	1.8 gm.	27 gr.	5.5 gm.	80 gr.
Glycin	——	——	11.0 gm.	¼ oz. 50 gr.
Water to make	1000 cc.	32 oz.	1000 cc.	32 oz.

Agfa 120 for soft results: For use, dilute one part stock solution with two parts water.

Agfa 130 for contrast results: For use, dilute one part stock solution with one part of water. Greater contrast can be obtained by using the developer full strength.

Either of these developers may be used alone or the print may be partially developed in one and then transferred to the other until development is complete. Generally, however, the developers are best employed in conjunction with each other.

Stop Baths.—Upon removal from the developer, the print should be drained briefly and rinsed thoroughly in a stop bath prepared by adding 1½ ounces of acetic acid (28%) to 32 ounces of water (45 cc. acetic acid to 1000 ccs. of water). The use of a stop bath reduces the risk of stains and lengthens the useful life of the fixing bath by neutralizing the alkali of the developer and preventing the oxidation of the developing agent. After a thorough rinse, the print is transferred to the fixing bath. Prints should not be allowed to remain in the stop bath for more than one or two minutes or the quality of the image may be affected.

[8] *Agfa Diamond,* Jan. Feb. 1940, p. 10.

Fixation of Prints.—It has been conclusively proved that the time required for the fixing of prints is much less than for negative materials.[9] There are four reasons for this:

1. The smaller grain size of papers as compared with negative materials.
2. The thinner emulsion coating and lower concentration of silver halide.
3. The greater solubility of silver chloride as compared with silver bromide and silver iodide.
4. The porous nature of the support which allows free access of hypo from both sides.

The time required for fixing in a *fresh* fixing bath depends upon the paper, the concentration of hypo, and the composition of the fixing bath, but is seldom over one or two minutes. The customary ten to fifteen minutes is justified, however, when prints are fixed in quantities and in a used fixing bath.

Owing to the smaller quantity of silver halides per unit area, a given quantity of fixing bath will fix more prints than films. However, there is no ready means of determining from the prints themselves whether or not the bath is in good condition; hence it is important to be on guard against using the bath beyond the limits which result in thorough fixing. For an acid fixing and hardening bath with a hypo concentration of 25%, this limit is approximately 50 8 × 10 prints per gallon, or an equivalent in other sizes.[10]

The use of two fixing baths is even more important than in fixing negative materials since (1) there is greater tendency to overwork the fixing bath in fixing prints, and (2) the proper fixing of prints depends upon keeping the prints in circulation during fixing to ensure access to hypo. The use of two fixing baths necessitates some handling of the prints in transferring from the first to the second bath and this in itself is an added guarantee of proper fixing.

Long fixation is harmful, particularly with a fresh fixing bath, as the relatively fine-grained image is slightly soluble in strong hypo, especially in an acid condition; thus prolonged fixing results in a reduction in the depth of the shadows and highlights which appear "eaten away." Longer fixing times by favoring the retention of the hypo by the paper base, necessitate longer washing.

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[9] Warwick, *Amer. Phot.* 11 (1917) 639. Lumière and Seyewetz, *Brit. J. Phot.* **71** (1924) 108

[10] For methods of testing fixing baths, see p. 358.

Washing of Prints.—It is often assumed that prints are more quickly washed than negatives because of the porous nature of the base which will allow elimination to take place from both sides. This, however, is not true, and prints in reality require longer washing for an equal degree of elimination from hypo than do negatives. This appears to be due to the retention of small traces of hypo by the baryta base coating of the paper.

Hickman and Spencer found[11] that extremely long washing times are required for the removal of hypo from papers and Crabtree, Eaton and Muehler, after a detailed investigation of the subject, concluded that prints cannot be washed entirely free from hypo within a reasonable length of time unless a hypo eliminator is used.[12]

The following hypo eliminator is advised:

KODAK HE–1

Hypo Eliminator Solution for Professional and Amateur Use

	Metric	*Avoirdupois*
Water	500.0 cc.	16 oz.
Hydrogen Peroxide (3% solution)	125.0 cc.	4 fl. oz.
Kodak Ammonia (3% solution)	100.0 cc.	3¼ fl. oz.
Water to make	1.0 liter	32 oz.

To make 3% ammonia, dilute 1 part of 28% ammonia with nine parts of water.

Directions for Use: Wash the prints for about 30 minutes at 65° to 70° F.[13] in running water which flows rapidly enough to replace the water in the vessel (tray or tank) completely once every 5 minutes. Then immerse each print about 6 minutes at 70° F. in the Hypo Eliminator Solution (Kodak HE–1), and finally wash about 10 minutes before drying.

Life of Kodak HE–1 Solution: About fifty 8-inch × 10-inch prints or their equivalent per gallon (4 liters).

Tests for the presence of hypo can be made by any of the usual methods (p. 367) but for prints the silver nitrate test is the most suitable.

With some papers, the use of this hypo eliminator may lead to a slight change in tone. In this case, add 15 grains of potassium bromide to each 32 ounces (1 gram per liter) of the solution. The slight yellowing of the whites may be minimized by immersing the prints in either a 1% solution of acetic acid or a 1% solution of sodium sulfite for two minutes upon removal from the hypo eliminator.

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[11] Hickman and Spencer, *Phot. J.* **64** (1924) 539.

[12] Crabtree, Eaton and Muehler, *J. Phot. Soc. Amer.* **6** (1940) 6.

[13] For lower temperatures, increase the washing time. Double the washing time should be used when double-weight prints are treated.

Drying Prints.—Prints on matte or semi-matte papers may be dried face up on blotters or on stretchers covered with cheese cloth or muslin. As prints left on the stretchers until bone dry will curl badly, they are best removed when nearly dry and placed between blotters and under pressure until dry.

A very satisfactory and convenient method of drying prints, except on glossy papers, is in a photo-blotter roll. This consists of a cloth-surfaced blotter, a plain blotter, and corrugated cardboard. The damp prints are laid face down on the cloth-surfaced blotter and covered with the plain blotter, then rolled up in the corrugated cardboard and fastened with a string or rubber band. The roll may be stood on end on the top of a radiator or hot-air register, or laid on its side with one end facing an open window. Prints dried in such a roll come out smooth and with a slight outward curl.

Prints on glossy papers are usually dried on squeegee tins or on glossy print driers.

There are two kinds of squeegee tins: the black enameled ferrotype plates and the chromium plates. The latter are more durable, scratch less easily, and last longer. There is also less tendency for prints to stick to the plate, particularly when dried by heat.

In either case, the plates should be cleaned frequently with warm water to remove any particles of gelatin which may have been left on the plate when the prints were removed. It is not necessary to use a polishing solution each time the plate is used, but to prevent prints from sticking, it is well to polish the plate every day or so. A good preparation for this purpose may be made by dissolving 10 grains of paraffin in one ounce of benzine. Any one of the many commercial preparations may be used instead if desired. Wet a tuft of cotton with this solution and go over the plate thoroughly; then polish off with a soft cloth such as canton flannel. There should be no visible trace of the solution left on the plate or the prints will have a greasy appearance.

When ready for use, the plates should be placed on a drainboard or in the sink and sprayed with water to remove dust or lint; the more water on the plate the less likely air bells are to form beneath the print and the less danger of prints sticking to the plate.

Where heat is used in drying prints on chromium squeegee plates, it is sometimes advisable to soak prints in a glycerin solution, 8 to 10 parts of water to 1 part of glycerin, for 5 minutes before placing them on the tins. This prevents prints from becoming brittle when dry and from cracking if run through a print straightener.

Prints should be taken directly from the wash water and, without draining, placed face down on the ferrotype plates, being careful to avoid air bells which will cause dull spots by preventing perfect contact. A slight pressure with the finger in the center of each print will prevent sliding.

Prints on squeegee tins may be allowed to dry normally or, if time is limited, drying may be hastened by using an electric fan or the moderate application of heat.

It is not advisable to dry prints too rapidly or at a temperature above 150° F., as the gloss and color of the prints will be affected. Rapid drying may result in the formation of drying marks or circles on the prints, and a ground-glass or check effect on the surface of the plates.

If prints adhere to the plate so that they cannot be removed, it may be due to one or more of the following causes:

1. The plate was not properly cleaned and polished.
2. The surface of the print was softened by prolonged washing, by washing in warm water or was insufficiently hardened because of an exhausted or improperly compounded fixing bath. Use a fresh acid fixing and hardening bath at a temperature not higher than 70° F. (21° C.).
3. The prints were dried at too high a temperature and without sufficient circulation of air. Avoid heat in drying and place the tins where there will be a good circulation of air.

Equipment for Processing Prints in Quantity.—Fig. 319 shows a developing machine widely used in photofinishing. The exposed prints are placed on the moving belt at the left. This leads to the "doping" mechanism which, operating without attention on the part of the operator, immerses the print in the developing solution which is contained in the large tray in front of the operator. In the developing solution, the prints proceed from left to right along the length of

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Weyde—Preventing Loss of Brilliance in the Hot-Drying of Prints. Phot. Ind. **36** (1938) 528.

Kieser—Preventing the "Burning" of Images with Hot-Drying. Phot. Ind. **36** (1938) 169.

Trieb—High Gloss Prints. Phot. Chronik. **43** (1936) 439, 450, 459; and **44** (1937) 14, 23, 29.

the tray in front of the operator who removes each print from the developer, when it has reached the proper depth, and transfers it to the stop bath on the other side of the partition at the right. This machine makes it possible for a single person to develop from 700 to 800 average size amateur prints per hour.

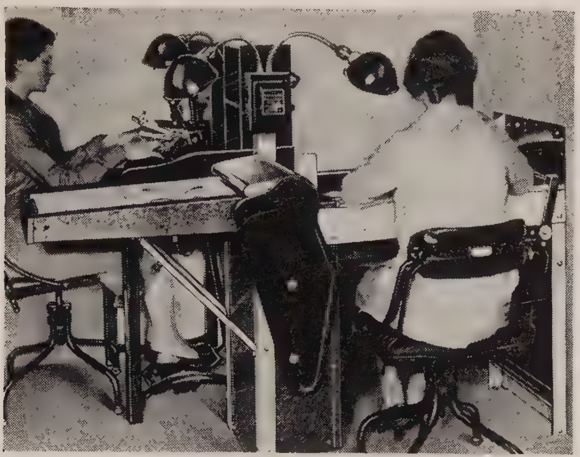

Fig. 319. Apparatus for Developing Prints in Quantity. (Pako Corporation.)

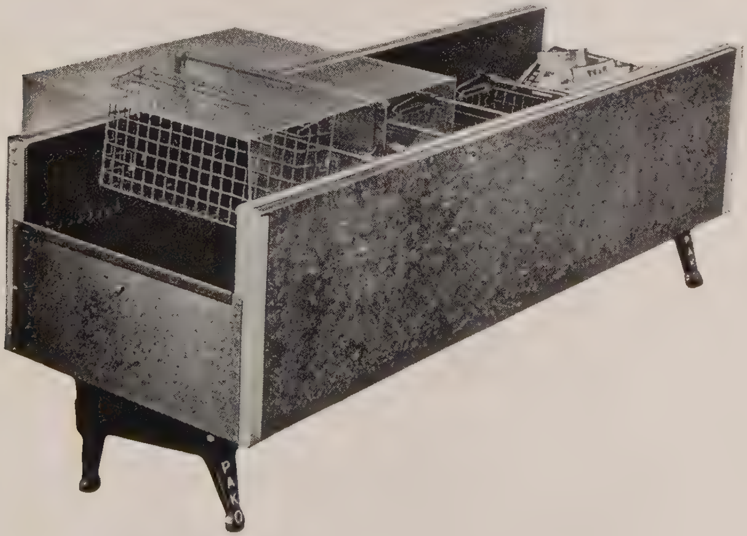

Fig. 320. Apparatus for Automatic Handling of Prints Following Development. (Pako Corporation.)

In Fig. 320 is shown a machine for the automatic handling of prints in the stop bath, the fixing bath and in washing. This machine consists essentially of a number of trays for the processing solutions and for washing all enclosed in a sink which, through power supplied by an electric motor, is rocked back and forth so as to keep the prints in the various baths separated and on the move constantly. Within these trays, the prints are contained in baskets as shown at the left. The prints on these baskets are automatically transferred from one tray to another at given time intervals so that the prints, after having been placed in the stop bath, require no further attention until ready for drying. The capacity of this machine is approximately 1000 average size amateur prints per hour.

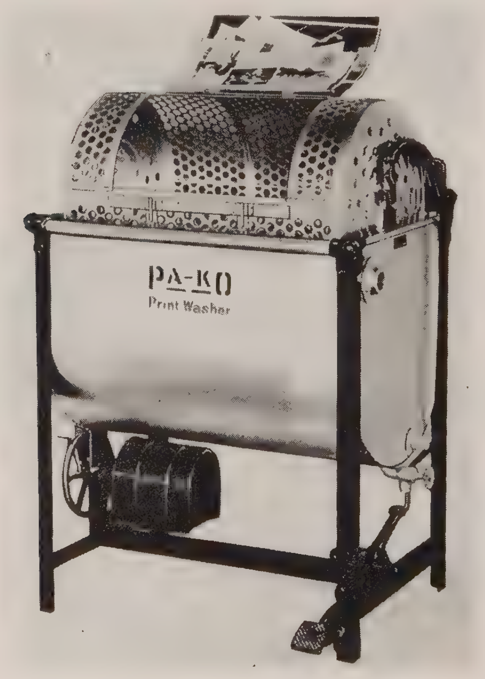

Fig. 321. Motor Driven Print Washer.

So far as efficiency is concerned, it is doubtful if any means of washing prints is superior to the use of a fairly large tray (16 × 20 or 20 × 24) fitted with an Eastman Automatic Tray Siphon (Fig. 321a). The water entering the tray makes a complete circuit, keeps the prints on the move and well distributed, and is drawn off through the siphon; the water in the tray is thus changed every few minutes. Few washing devices provide so rapid changes of water.

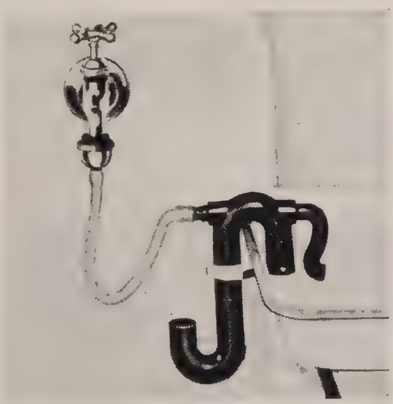

FIG. 321a. Eastman Syphon Washer.

For large batches of prints the cylinder cage type of washer (Fig. 321) in which the prints are placed in a cage which is revolved either

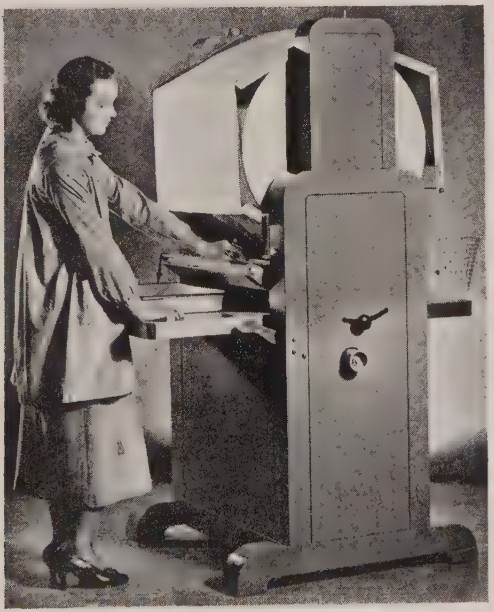

FIG. 322. Belt Drier for Glossy Prints (Eastman).

by water power or an electric motor is more suitable, although it is not particularly efficient either from the standpoint of rapid water changes or keeping the prints well separated.

The most common form of print drier is that in which the prints are placed on a belt which passes over a heated drum revolved by a motor. There are several different types; some with a single belt and others with two. Some are adapted for semi-matte or matte prints, others for gloss prints. In the latter, the surface of the drum consists of polished chromium steel, and the prints are dried with the emulsion side in contact with the drum.

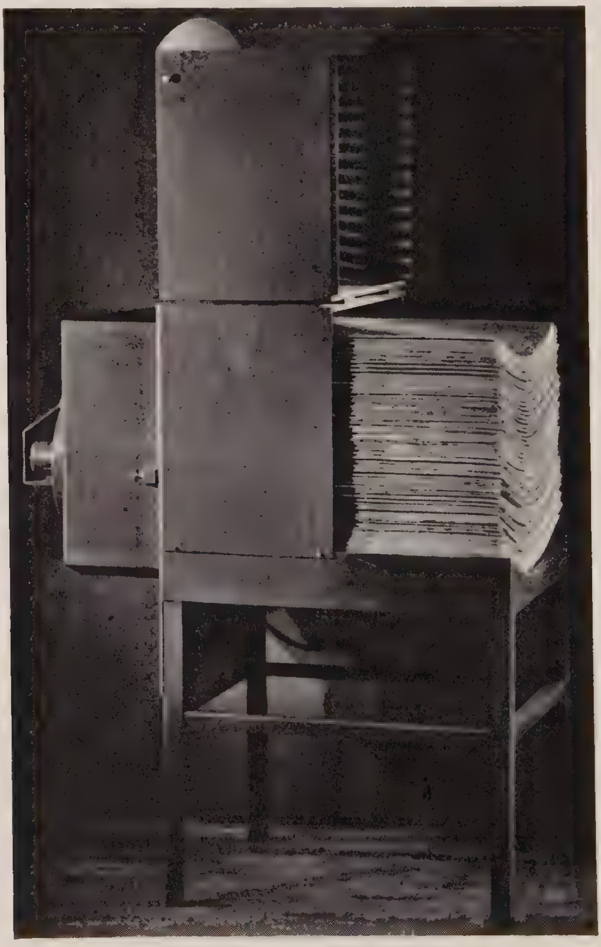

Fig. 323. Drier for Matt Prints.

The drier shown in Fig. 323 is designed for portrait and commercial prints on semi-matte or matte papers. The prints are placed between linen faced blotters which, in turn, are placed between sheets of corrugated board. Warm air supplied by an electric heating unit is then blown through the openings in the corrugated boards by means of the electric fan shown at the left.

Rush Prints.—Where time is an important consideration, prints may be made from the negative as soon as it has been fixed by covering the emulsion surface with a sheet of thin celluloid, cellophane, or Kodapak. The negative will not be damaged if it has been thoroughly hardened in a properly compounded acid fixing and hardening bath, unless, of course, it is allowed to become quite warm.

The time required to dry prints may be reduced slightly by immersing the well-washed prints for about one minute, or until the paper assumes a transparent appearance, in methyl alcohol and then drying by heat. Less heat is required and the color of the image is not altered to the same extent as when drying is forced by the use of heat.

For still more rapid drying, the alcohol adhering to the surfaces of the print may be burned off. This, however, is not recommended except where speed is the primary consideration.

Prints for Reproduction.—The coarse half-tone screens (60–70 lines per inch) necessary for newspaper reproduction destroy fine detail and delicate gradations of tone. The picture, therefore, should be built up of distinct, clear-cut masses of light and shade. A light or medium tone background is better than a dark black one as black backgrounds are difficult to print on high speed newspaper presses. Prints for newspaper reproduction should be a trifle lighter than would be regarded as correct for other purposes, because of the tendency in newspaper printing for the half-tone dots to "fill in," which results in a reproduction darker than the original.

The print should be black or blue-black. Prints with a greenish or olive-black color are no longer desired by the photo-engraver. It should be on glossy paper, squeegeed, and have at least ½ inch margin. A print larger than the reproduction is desirable, but if enlarging is resorted to, the print must be critically sharp and clear.

In printing upon coated papers, finer line screens are used (80 to 145 lines per inch) and the detail and gradation of tone in the original can be more accurately reproduced than in newspaper work.

Prints for reproduction in publications using coated or calendared paper should have a full scale of gradation and not too much contrast. Contrast in the subject is desirable, but artificial contrast which is produced photographically through over-development of the negative or the use of a hard paper is to be avoided. A print with chalky highlights and dark shadows will, in the ordinary course of events, become still more contrasty when reproduced.

In rotogravure and photogravure, the best results are secured from photographs with clean, brilliant highlights and good rich blacks. Since both processes tend to increase contrast, the original should be rather softer than that for half-tone reproduction.

Improvement of the Print by Local Shading During the Exposure.—The improvement of the print through shading or otherwise altering the amount of exposure which a portion of the image receives and so controlling the values of the print is known as dodging.

The simplest method of dodging consists in shading, during the exposure, with an opaque card held in the hand and kept in motion to prevent a sharp edge. Shading may be utilized to hold back an area which prints too dark or to increase the exposure in the case of an area which prints too light. Small areas which print too light may be printed by cutting an opening of the proper size and shape in a piece of cardboard and using this to shade the rest of the negative so that it will not be over-exposed while the additional exposure is being given for the denser portion. A small area which prints too dark can be held back with a card of the proper size and shape attached to a piece of wire and kept in motion during the exposure so that the wire will not show.

It is very difficult to shade negatives in this way on many printing machines because the opaque platen of the printing machine prevents one from seeing what is being done. The principal objection to shading as a means of controlling local values, however, is that it is difficult to make a number of prints exactly alike.

If the negative is on glass, the back is covered with ground-glass substitute and areas which are to be lightened are gone over on the back with a soft lead pencil. If the negative is on film, a sheet of clear glass is flown with ground glass substitute, the back of the film negative attached to the clear glass side, and the density of the areas to be lightened built up with a soft lead pencil. For larger areas, crayon sauce, obtainable from artist supply stores, may be applied with paper stumps or a small wad of cotton. Instead of crayon sauce, many prefer a little ordinary blue water color applied with a brush. Unless the area is to be held back considerably, the blue color will probably be sufficient; yellow may be used sparingly for very thin areas. Areas which are to print darker may be improved by applying a little vaseline to the ground glass.

Great accuracy is not necessary since the thickness of the glass so diffuses work on the ground side that minor irregularities are smoothed out.

Another method of control which is suitable for areas not too small consists in placing a sheet of tissue or transolene (obtainable from photographic supply houses) an inch or so below the negative and applying water, oil colors, or opaque (much diluted) to the paper beneath those portions of the negative to be held back. Openings may be cut in the paper to accommodate those portions of the negative which need more exposure.

Thin wads of cotton placed on a sheet of glass an inch or so below the negative may be used to good advantage in some cases. A few printers use sand in a glass bottom tray in much the same manner.

Still another method (and a very convenient one) is to cut openings in onion-skin paper in such a way as either to hold back certain parts of the negative or to make them print darker, whichever is desired. The negative is placed on the printing machine and the area to be held back (or to be printed darker as the case may be) is outlined on a sheet of paper placed over it, using a wax pencil. The outline is made a trifle smaller than the area to be held back. Now take the point of a sharp knife and cut out the paper along the outline, making a saw-tooth edge. Place the cut-out paper mask on one of the clear glass shelves below the negative and center the negative over it so that the areas to be printed darker will be directly over the cut-out portions of the paper. The negative is now attached to the glass of the printer with Scotch tape and the print made. The sharpness of the outline may be controlled by placing it at different distances from the negative—the nearer it is to the negative, the sharper the shading.

Vignetting.—To produce a vignetted print (that is, one in which the image fades gradually into white paper) a subject with a white background is necessary.

To make a vignetted print, proceed as follows: Attach the negative to the glass of the printing machine (or printing frame) using two short pieces of cellulose tape. Place over the negative a sheet of clear glass and outline on this glass, using a wax or china-marking pencil, the portions which are to be vignetted. Remove the glass, and place over it a sheet of yellow-orange or "post office" paper and trace the outline on the paper. With the point of a knife tear out the inner portion leaving a jagged, saw-tooth edge. The rougher the edge and the longer the "teeth" of the saw, the better. Now place the cut-out mask on one of the sheets of glass several inches from the negative. The greater the distance between the mask and the negative, the softer will be the edge.

Some printers make vignetted prints by means of a glass-bottomed tray and sand. The black sand used by sign painters is best, but ordinary fine-grain sand is satisfactory. To distribute evenly the sand, the tray is shaken and then placed on one of the glass shelves directly beneath the negative. A soft brush is used to "shape up" the opening in the sand to produce the desired effect. By having the layer of sand thin along the edges, the light coming through the sand will produce a graded edge. The remainder of the layer should, of course, be sufficiently thick to prevent light from reaching the paper.

A vignetted effect may be produced on the negative with an air brush using a fine grade of lamp black or non-actinic color.

Reduction and Intensification of Prints.—Generally speaking, the action of the various reducers is the same as with negative materials.[14] The permanganate reducer acts nearly proportionally, while iodine cyanide is perhaps the best subtractive reducer because it is non-staining. For super-proportional reduction, persulphate alone appears suitable. In practically all cases it is necessary to use a diluted solution to keep the process under control.[15]

For local reduction, iodine cyanide is especially suitable as it is non-staining and does not change the color of the image. The "'waxy" appearance of the reduced area may be removed by washing the print for 5 to 10 minutes, fixing for 5 minutes and washing for 15 to 20 minutes.

Dry prints may be reduced with a spirit-soluble reducer composed of iodine and thiocarbamide in methyl alcohol.[16] In addition, there is no continuing action to result in over-reduction and no tendency of the reducer to spread over into portions where it is not wanted. Two stock solutions should be prepared:

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[14] Jones and Fawkes, *Brit. J. Phot.* **68** (1924) 275.

[15] Staude, *Phot. Rund.* **73** (1936) 429.

[16] Greenall, *Brit. J. Phot.* **73** (1926) 73, 383.

A—Iodine	20 gr.
Methyl alcohol	1 oz.
Shake now and then until dissolved	
B—Thiocarbamide	40 gr.
Water to	1 oz.

For use take equal parts of *A* and *B*. For areas requiring but little reduction, this may be diluted with an equal part of water.

The dry print is pinned down by the corners to a board and the reducer applied to the area to be reduced with a water color brush of appropriate size just wet with the solution. In the other hand must be a larger brush or tuft of absorbent cotton charged with the methyl alcohol which is applied to the print immediately not waiting to see if reduction has gone far enough. The excess alcohol is next blotted off and the operation again repeated if the first has not been sufficient. As soon as reduction is complete, dip the print in hypo (without previous washing) for a few minutes; then wash and dry as usual.

Permanence of Prints.—The fading of silver images is the result of the partial conversion of the silver of the image to silver sulfide from (1) the decomposition of hypo left in the image from insufficient washing, (2) insufficient fixation which results in the formation of complex silver sodium-thiosulfates which decompose to form silver sulfide, or (3) to attack by hydrogen sulfide, sulfur dioxide and other gases generally present in the atmosphere, particularly in industrial localities. Fading from all sources, but particularly the last named, is greatly accelerated by high temperature and by moisture.

Prints made for historical or other records should be thoroughly fixed in a fresh fixing bath and thoroughly washed using a hypo-eliminator (p. 369) to ensure the complete removal of hypo.[17]

Fading, due to external agents, may be reduced (1) by sulfide or gold toning,[18] (2) by covering the print with a water-proof lacquer, and (3) by dry mounting rather than the use of water-miscible adhesives. The latter, being hygroscopic, tend to contribute to fading by attracting moisture to the image. Gold toning is generally preferable to sulfide toning, as the change in the color of the print is so slight with many papers as to be unimportant. In using a lacquer, care should be taken to use only those which have been tested and found to be free of any deleterious effect on the image.

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[17] Crabtree, Eaton & Muehler, *J. Phot. Soc. Amer.* **6** (1940) 6.

[18] For a suitable gold toning formula, see p. 653.

Freytag—Factors Influencing Permanency of Prints. Phot. Chron. **44** (1937) 401.

CHAPTER XXIII

CONTACT AND PROJECTION PRINTING

In contact printing, as the name indicates, the sensitive paper is exposed in contact with the negative; in projection printing an image of the negative is formed on the paper by optical projection. The projected image may be larger than the negative (*enlargement*) or smaller (*reduction*). Projection printing is usually employed to make prints larger than the negative and hence is frequently termed *enlarging*.

Contact Printing—Exposing the Print.—When using a printing frame, the back is removed, a sheet of cleaned glass free from imperfections is placed in the frame, and the negative on this with the emulsion side up. The paper is then placed in the frame with its sensitized surface in contact with the negative, the back replaced and the springs clamped down. If white margins are desired, a mask should be placed either between the glass and the negative or the negative and

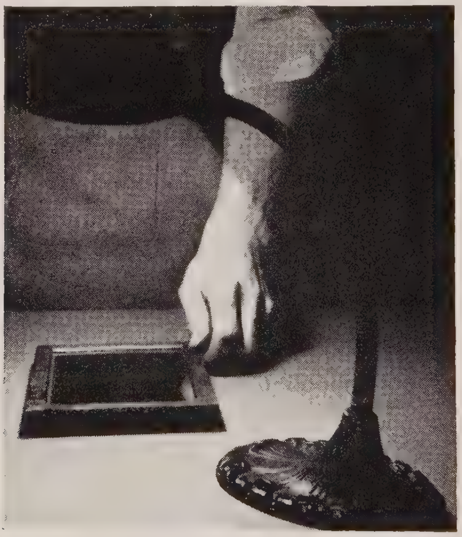

FIG. 324. A Reading Lamp Provides a Simple Means of Exposing Prints When Using a Printing Frame.

the paper. In the case of film negatives, the first position is preferable; with glass plates, the mask should be placed between the negative and the paper.

A convenient method of exposing is shown in Fig. 324. The distance between the lamp and the printing frame should be sufficient to illuminate the negative uniformly. This method of exposing is not as rapid or as convenient as a printing machine, but has the advantage of affording greater opportunities for the shading or "printing in" of portions of the negative requiring a different exposure from the rest.

The usual method of determining the proper exposure is by means of trial and error using test strips. See pages 598 and 635.

Printing machines may be broadly divided into four classes: (1) amateur, (2) professional, (3) photofinishing, and (4) those in which the required time of exposure is made automatically. At the present time, all printing machines of this last mentioned type are designed for photofinishing; however, the principles employed may be extended to other types in the future.

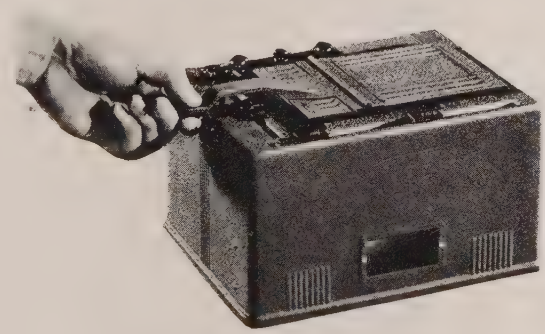

FIG. 325. Printer for Amateur Use (Eastman).

A typical printing machine designed for use by the amateur is shown in Fig 325. It is designed for printing from negatives 4 × 5 inches in size, or smaller, singly or in a roll, and has a 40 watt exposing light which is switched on and off with the lowering or raising of the platen and a ruby pilot light which burns continually. A masking device of four adjustable metal strips is provided for convenient masking of negatives of different sizes.

Printing machines for professional use are similar, but are designed for larger negatives (8 × 10, 11 × 14 and larger), are more ruggedly built and more attention is given to methods of changing the illumination for papers of different speed and shading, or otherwise controlling the exposure on different parts of the negative. In the example shown in Fig. 326, any one of three tungsten lamps, which may vary from 25 to 1000 watts, may be used according to the speed of the paper or the density of the negative by one simple movement of the fixture in which the three lamps are mounted. Sheets of plane or ground glass are placed below the heavy plate glass printing surface for shading material. In another example, the top of which is shown in Fig. 327, the printing head is hinged so that after making a general exposure in the

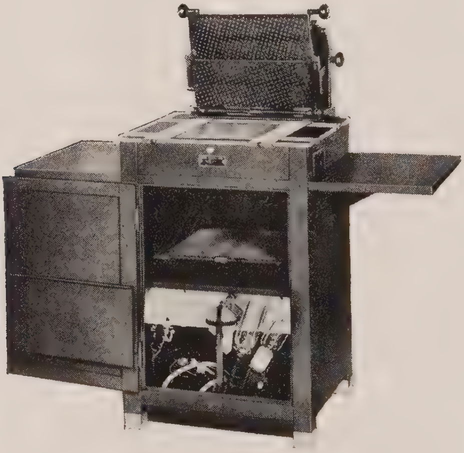

Fig. 326. Printer for Professional Use (Eastman).

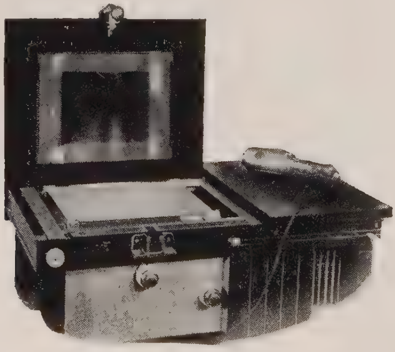

Fig. 327. Head of Pako Professional Printer Shown Raised to Permit Use of Spotlight Shown at Right for Local Printing.

usual manner, the top of the printer may be raised to the vertical position as shown, and dense areas on the negative "printed in" with the small hand-held spotlight at the right.

Printing machines for use by the professional photofinisher are designed for the rapid printing of amateur negatives either in a roll or singly. In the example shown (Fig. 328), the exposing platen is operated by a foot treadle so as to leave both hands free for manipulation of the paper and the negative. An adjustable numbering stamp places the order number on the back of each print. This enables the prints as they come from the driers to be classified by order numbers. In some cases, the machine is designed so that the exposed sheet of paper slides into a container which is removed at intervals and the accumulated prints developed; in other cases, the exposed sheet of paper slides on to a conveyor belt which takes it to the developer.

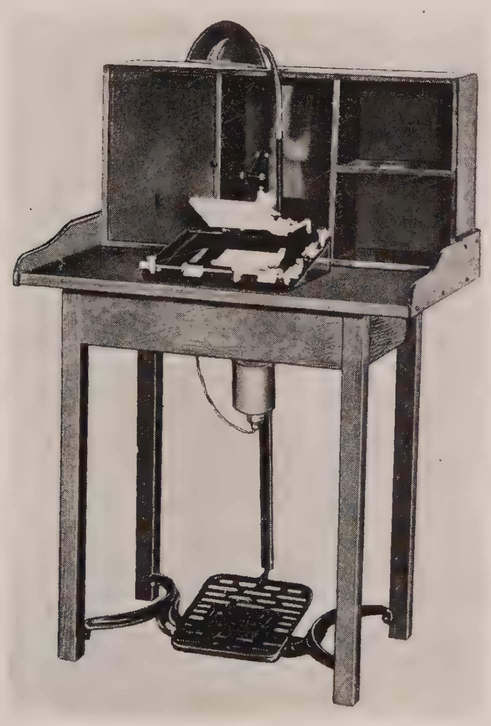

FIG. 328. Printer for Commercial Photofinishing. (Pako Corporation.)

Two common difficulties with printers are imperfect contact and uneven illumination. Imperfect contact may arise with use from the weakening of the springs and is sometimes due to buckled or warped negatives. Imperfect contact, particularly along the margins, is sometimes caused by placing the negative *underneath* rather than on the masking strips. Poor contact may be discovered by making a print from a negative having sharply defined detail throughout the image. A copy of a page of printed matter makes an excellent test plate. If poor contact is discovered, the springs should be adjusted or renewed. Lack of uniformity in illumination is sometimes the result of using a lamp for which the printer was not designed. The illumination over the printing area may be checked by making a brief "flash" exposure on a sheet of contrast paper without a negative. If the exposure is not too great, any unevenness in illumination will be apparent upon development. Sometimes the illumination can be improved by the addition of a sheet of ground or opal glass. In some instances, the use of a smaller lamp or moving the position of the lamp will improve matters.

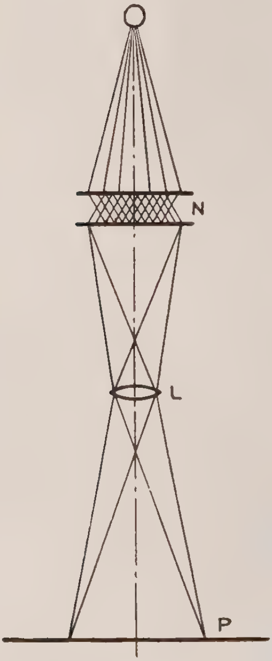

Fig. 329. Principle of Projection Printing.

Projection Printing. — In projection printing, the light rays passing through the negative, *N* (Fig. 329), and the lens, *L,* are brought to a focus on the sensitive paper, *P,* forming an image the size of which depends upon the focal length of the lens and the relation of the negative-lens distance and the lens-to-paper distance. These distances are the so-called conjugate distances (see p. 623), and are usually designated as v and u respectively. When u is greater than v, the projected image is larger than the original and the resulting image is termed an enlargement. When v is greater than u, the projected image is smaller than the original and the print is termed a reduction. The distances u and v are readily found from the following equations:

$$v = \left(\frac{m + l}{m}\right) f,$$

$$u = (m + l)f,$$

where m = magnification of the image (i.e., ratio of negative to projected image) and f = focal length of the lens.

The apparatus employed for projection printing consists essentially of the following parts:

1. A light source of sufficient intensity and suitable characteristics.
2. A light-tight housing to enclose the light source.
3. A reflector, condensing lenses, or both, to illuminate uniformly the negative.
4. A holder for the negative.
5. A projection lens with a bellows, sliding tube, or other light-tight, adjustable connection with the negative.
6. Means for focusing the image.
7. A standard to support the projection unit and provide for its movement up and down.
8. An easel to hold the sensitive material in place for the exposure.

Light Sources for Projection Printing.—Electric sources have long displaced all others; incandescent tungsten lamps are now by far the most widely employed; gaseous conductor tubes, such as the mercury vapor arc and fluorescent tubes, are in use to a limited extent, but the electric arc is no longer in general use.

While clear glass lamps are used frequently, the trend is towards the use of photoenlarger lamps having an opal glass bulb, even in projection apparatus fitted with condensing lenses. Some photoenlarger lamps are of the overvolted, or photoflood, type and have a relatively short life. This is not in itself a serious disadvantage except that the illumination falls off rapidly as the lamp approaches the end of its life; variations in exposure, therefore, are more frequent than with lamps having a longer life.

An important consideration in the use of incandescent filament lamps of any kind is the variation in the intensity of illumination, and therefore in exposure, with comparatively small variations in voltage (page 172). For work demanding high precision, as in printing from color separation negatives, it is important that means be provided for maintaining an electrical supply of constant voltage. Manually controlled devices are generally adequate, but automatic voltage regulators are more convenient and more desirable, if the fluctuations in voltage are frequent.

A second important consideration in the use of incandescent tungsten lamps is the dissipation of the heat in such a way that the negative is not likely to be damaged. A large proportion of the radiant energy output of an incandescent filament lamp is in the infra-red (heat) region. This radiation, unless prevented from reaching the negative by heat-absorbing glass, may result in the buckling or melting of film negatives, or the cracking of glass plates, on long exposure.

Mercury-vapor arcs, such as the well known Cooper-Hewitt lamp, and fluorescent tube lamps have several advantages as compared with incandescent filament lamps. The tubes form a more extended source of light with greater diffusion, thus simplifying the problem of obtaining uniform illumination and lessening the contrast with which retouching, scratches and other defects on the negative are reproduced in the print. Unlike incandescent lamps, the fluorescent lamp and the mercury-vapor arc generate but little heat; they also show less variation in illumination with voltage changes. On the other hand, the high degree of diffusion and the abundance of shortwave radiation result in images of lower contrast than when incandescent lamps are used. The difference is more marked with mercury-vapor arcs than with fluorescent lamps. Finally, a minor disadvantage is that exposures cannot be made by turning the light on and off as the lamp does not reach full intensity for some time after the current has been applied; hence, the lamp must be allowed to burn continuously and the exposure made by means of a shutter or cap.

Illumination of the Negative.—Incandescent lamps are usually used singly in a reflector, generally parabolic in shape, which also forms the light-tight housing confining the light to that passing through the negative. The interior of the reflector is usually given a diffuse (matt) reflecting surface, but is sometimes silvered. The silvered reflector is the more efficient, but is also the more critical from the standpoint of obtaining uniform illumination. In either case, the light from the lamp is directed onto a diffusing screen of opal or ground glass, which thereupon becomes the actual source of light illuminating the negative. The problem of securing uniform illumination is rendered somewhat simpler if the light source is relatively large and diffused, hence the preference for lamps with opal glass bulbs. With large negatives, it is frequently necessary to resort to the use of diffusing screens of sand-blasted glass heavily blasted in the center and gradually diminishing towards the margins in order to obtain uniform illumination.

The brightness of the image under these conditions depends upon: (1) the illumination on the diffusing screen, and (2) the angle subtended by the projection lens at the easel. This in turn depends: (1)

on the clear diameter of the objective, and (2) on the scale of enlargement (or reduction) increasing with the diameter of the lens aperture and decreasing with the scale of enlargement.

Since, with diffuse reflected illumination, only a small part of the light transmitted by the negative is intercepted by the lens, this method of illumination is wasteful of light. Through the use of condensing lenses, however, it is possible to increase the amount of light passing through the lens and thus increase the brightness of the image on the easel, thereby reducing the time of exposure—an important consideration with slow papers, dense negatives or large scale projection. The function of the condensing lenses is to image the light source in the entrance pupil of the projection lens (Fig. 330) resulting in more efficient utilization of the light. The condensing lens system employed for projection printing consists of two plano-convex lenses slightly greater in diameter than the diagonal of the largest negative and placed with their convex sides facing.

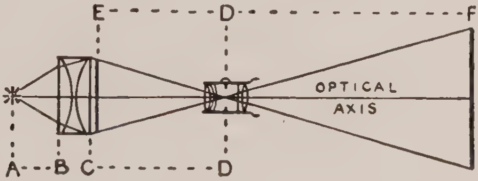

FIG. 330. Optical System of a Projection Printer with Condensing Lenses.

When condensing lenses are used without a diffusing medium, the maximum efficiency is obtained when the diameter of the light source is no greater than that of the aperture of the lens and when the light source is located at the point on the optical axis at which its image —formed by the condensing lenses—is located at the principal nodal plane of the projection lens. If we ignore the exact nodal planes, this means that the distances *AB* and *CD* (Fig. 330) are conjugate foci of the condenser, while the distances *ED* and *DF* are conjugate foci of the projecting lens. As the degree of enlargement is altered, the distances *ED* and *DF* will vary according to the laws of conjugate foci (See Chapter III). With every variation in $ED:DF$ there will be a corresponding variation in $AB:CD$, so that in order to keep the image of the light source in its proper place at the principal nodal plane of the projecting lens, the distance *AB* must be varied each time the degree of enlargement is altered.

However, if a lamp with an opal glass bulb is used, or a sheet of ground or opal glass placed between the light source and the condensing lenses, it is no longer necessary to change the position of the light source with every change in the scale of enlargement. This is true, however, only within certain limits. A condensing lens system which fills the aperture of a projection lens of given focal length, more than fills the aperture of a lens of shorter focal length and fails to fill that of a lens of longer focal length. Hence, if a projection printer is designed for use with lenses of different focal lengths, the maximum efficiency will be obtained with each lens only if the position of the light source is changed for each lens or if condensers of the proper focal length are substituted with each change in the projection lens. The latter method is usually followed since it relieves the user of the necessity of carefully re-focusing the light whenever the projection lens is changed.

Mercury-vapor arcs and fluorescent lamps, being extended sources, require only a suitably designed reflector and a sheet of ground, or opal, glass to produce uniform, well-diffused illumination. Sources of this type are especially suitable for projection printing equipment designed for large negatives.

Negative Illumination and Print Quality.—Adequate diffusion of the illumination on the negative is a very important factor in the production of prints of good quality. The diffuseness of the illumination on the negative affects (1) the contrast of the print obtained

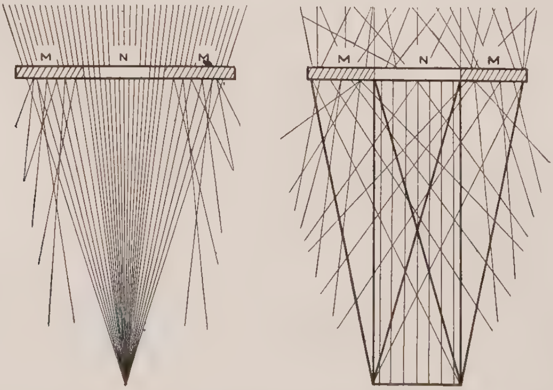

FIG. 331. Illustrating the Difference in Loss of Light from Scattering by the Densities of the Negative with (Left) Specular and (Right) Diffuse Illumination. (Bentley, *British Journal of Photography.*)

under given conditions, (2) the graininess of the image, and (3) the sharpness with which scratches and similar imperfections as well as retouching and any handwork on the negative are brought out in the print.

Fig. 331 [1] represents the conditions existing when a negative, represented by the letters *M N M,* is projected, at the left with specular light from a condensing lens system without diffusion, and at the right with diffused illumination. In the first case, the light reaching the negative is converging on the projection lens. The rays of light incident on the denser parts of the negative, m, are scattered by the silver particles. On the other hand, the rays of light incident on the portions where there are fewer particles of silver to scatter the light, will be transmitted with little or no loss from scatter. Thus, the differences in the light absorbed by the densities of the negative are increased by the light lost from scattering. With diffuse illumination, however, the loss from scatter is more nearly uniform and the density differences are not increased as with specular illumination.

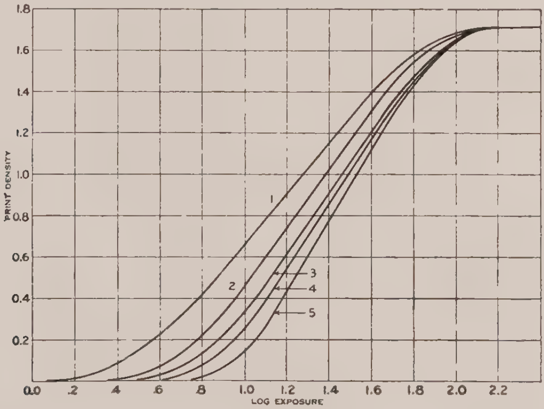

FIG. 332. Curves of a Projection Paper Showing the Effect of Variations in the Diffuseness of the Illumination on the Shape of the *D* log *E* Curves.

The effect of variations in the diffuseness of the illumination of the negative on the contrast of the image is shown in Fig. 332.[2] The *D* log *E* curve, marked 1, was obtained on a given paper with light diffused with pot opal glass a short distance from the negative. Curves

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[1] Bentley, *Brit. J. Phot. Almanac* (1931) 169.

[2] Tuttle, *J. Opt. Soc. Amer.* **24** (1934) 279.

2, 3, 4, 5 are for the same paper but with flashed opal glass, glass ground on both sides, ordinary ground glass (ground on one side) and clear glass respectively. The step tablet used in this case was on fine grain negative material. The use of a coarse grain negative material would result in curves with still greater differences. The difference in contrast between curves 1 and 5 is approximately equal to one contrast grade of paper.[3]

Investigations by Tuttle[4] indicate that the improvement as regards graininess and elimination of scratches and other surface effects is progressive with increasing diffusion up to a diffusion factor of approximately 50% (Fig. 333) beyond which the gain is very slight and the loss of light and the lower contrast of the image are of more con-

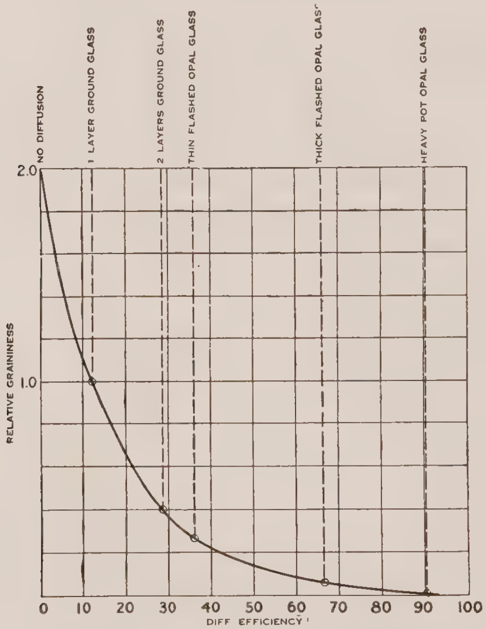

FIG. 333. Curve Showing Relation Between the Diffuseness of the Illumination on the Negative and the Relative Graininess of the Projected Print.

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[3] The control of the contrast of the image in projection printing by varying the degree of specularity in the illumination on the negative has been discussed by Naumann and by Benedict. Naumann, *Brit. J. Phot.* **84** (1937) 834. Benedict, *Camera Craft,* — (1936) 275.

[4] Tuttle, *J. Opt. Soc. Amer.* **24** (1934) 279.

sequence than the improvement in image quality. In general, as the scale of enlargement is increased, the need for a high degree of diffusion in illumination increases.

The Negative Carrier.—The negative carrier should (1) hold the negative flat, (2) provide for the convenient changing of negatives and (3) for the centering of any desired portion of the negative about the optical axis of the projection system. With film negatives, the first requirement may be met by placing the negative between glass plates. The glass, however, is difficult to keep perfectly clean and interference patterns (Newton's rings) are formed if the film and glass are not in contact with one another. For this reason, negative carriers in which the glass is dispensed with and other means provided for holding the negative are much to be preferred. Unfortunately, it is difficult to hold negatives in the larger sizes flat except with glass.

The Projection Lens.—Lenses for projection printing should be well corrected for spherical and chromatic aberration and have an anastigmatic lens field. It is important, moreover, that these corrections be for a plane close to the lens as the lens to image distance is less than that for which general-purpose lenses are corrected. (Process lenses are an exception.)

Much of the better grade apparatus now on the market is fitted with lenses designed especially for projection, and projection anastigmats are available from several opticians, but high grade anastigmatic lenses of medium aperture are usually adequate. In most cases, it is preferable to mount the lens so that the rays of light pass through it in the same direction as when used on a camera.

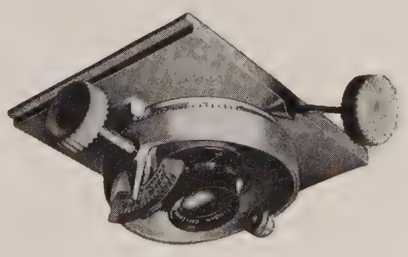

FIG. 334. Tilting Lens Front for Use on Projection Printer (Elwood).

Fig. 334 shows a lens front which enables the lens to be tilted at an angle when the negative or the easel is inclined for the purpose of correcting or introducing distortion.

The focal length of the lens required for projection depends upon

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BENDER—Contrast Control in Projection Printing. Phot. Ind. **37** (1939) 941; Phot. Tech. **2** (1940) March, p. 45.

ROEDER—Comparison of the Tone-Rendering in Contact-Prints and Enlargements. Phot. Ind. **37** (1939) 751.

the size of the negative to be covered and is usually approximately equivalent to, or slightly greater than, the diagonal of the negative.

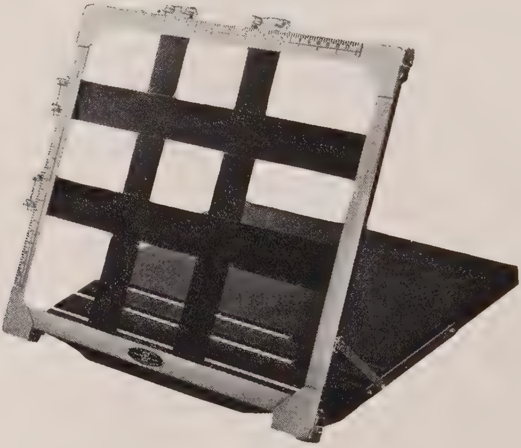

Fig. 335. Paper Holder (Easel) for Projection Printing (Albert).

The focal length of the lens has a bearing also on the equality of illumination—a lens of very short focal length may result in uneven illumination. Except for these two requirements, the focal length of the lens affects only the negative-to-lens and the lens-to-easel distances. These are conjugate distances and are readily determined from the usual formula.

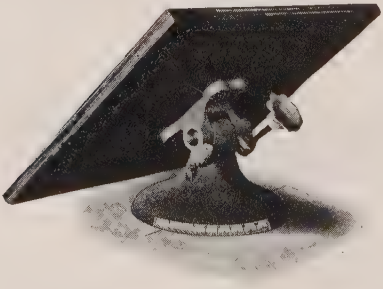

Fig. 336. Paper Holder (Easel) Designed to Facilitate the Placing of the Paper at an Angle to the Optical Axis to Correct or to Introduce Distortion in the Negative Image (Elwood).

Focusing.—On projection printing apparatus having a flexible bellows, focusing is ordinarily by rack and pinion. Frequently, both a coarse and a fine movement is provided. On apparatus without a bellows, the lens is usually mounted in a rotating sleeve and in other examples in a sliding tube actuated by a rack and pinion.

The Easel.—The easel should (1) hold the sensitive paper flat, preferably without glass, (2) provide means for inserting and removing the sheet of paper conveniently, (3) have adjustable, accurate blades for masking off undesired parts of the image and for producing white margins, and (4) provide means for readily determining the size of the print and the width of the margin. To correct distortion in the negative or to introduce distortion in the print for pictorial purposes, the easel should be designed so that it can be conveniently inclined at an angle to the optical axis of the lens. A typical easel with masking blades which serve also to hold the paper flat and in place is shown in Fig. 335, and another specially designed for convenience in using at an angle is shown in Fig. 336.

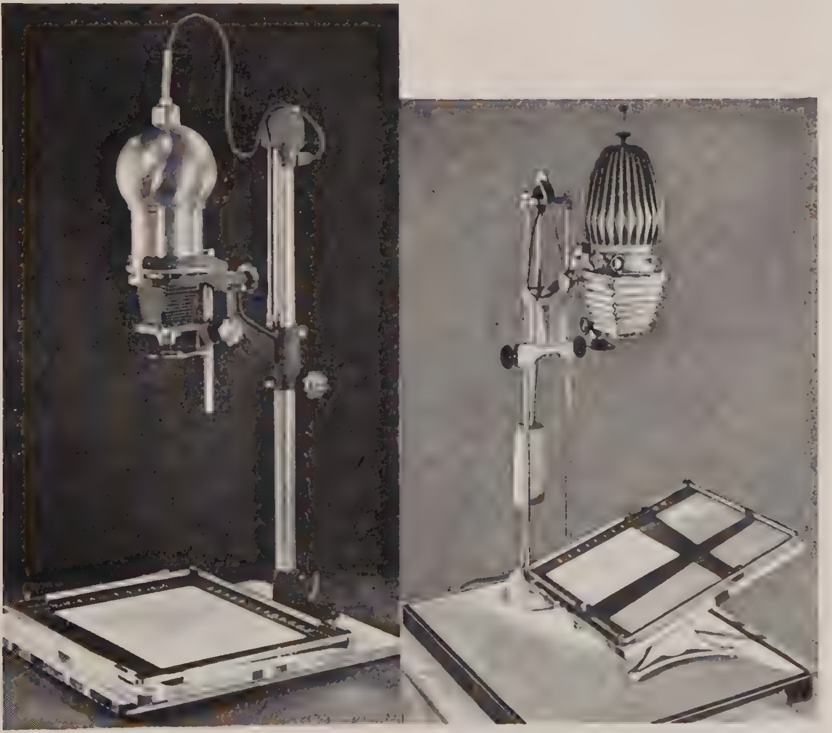

Fig. 337. Projection Printing Equipment. (Left) Kodak *Precision* Enlarger, (Right) Graflex *Variograph* Enlarger.

Projection Printing Equipment.—Two examples of projection printers typical of a large number for amateur use with negatives up to 2¼ × 3¼ or 3¼ × 4¼ are shown in Fig. 337. These, and most apparatus of this type, employ condensing lenses for efficient utilization of the light source which is almost invariably an opal glass photoenlarger lamp. Thus, through efficient utilization of the light, long exposures or lamps of high wattage are both avoided without sacrificing too greatly the diffuseness of illumination which is required for good print quality. Projection apparatus of this type ordinarily employs metal book-form negative carriers without glass and well corrected projection anastigmat lenses at apertures of $f/4.5$ or even larger. In many cases, lenses of different focal length are available for greater convenience with negatives of different sizes and condensing lenses of the proper focal length for each lens are provided to avoid the necessity of changing the position of the light source when changing from one lens to another. In several examples, a tilting negative carrier or lens is provided for producing special effects.

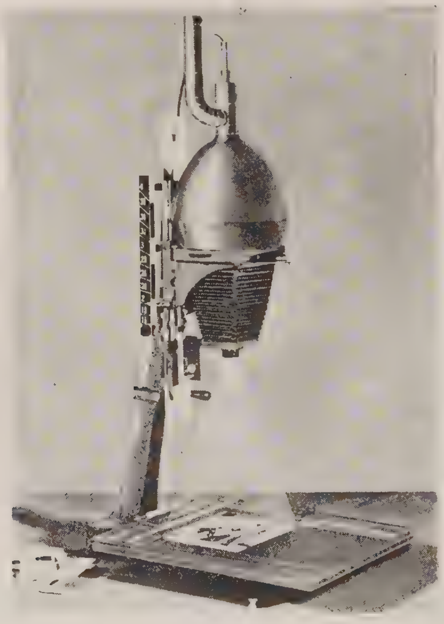

Fig. 338. Projection Printing Equipment. (Eastman Auto-Focus Enlarger 5 × 7.)

An autofocus projection printer of the type widely used by professional photographers for negatives up to 5 × 7 inches is shown in Fig. 338. Equipment of this type is rapid and convenient in use as it requires no focusing; the arrangements for automatic focusing, however, prevent the use of lenses other than that for which the apparatus is designed, and limit somewhat the range of magnification available. In the example shown, the range is from 1.5 to 4.0 times. Reductions to 1 to 2.75 the scale of the original are possible with an accessory reducing attachment. The light source is a frosted-tip, clear glass lamp in a parabolic shaped reflector with a matt-aluminum reflecting surface. Uniform illumination is obtained through the use of a sandblast diffusing screen placed directly above the negative. A sheet of heat absorbing glass is used to protect the negative and openings around the negative carrier and the air duct at the top of the reflector provide ventilation.

In Fig. 339 is shown a projection printer designed for exacting technical requirements with negatives up to 8 × 10 inches. This apparatus employs fluorescent lamps in a specially designed reflector and an opal glass diffusing screen. It is exceptionally stable, nevertheless convenient in operation, the raising and lowering of the camera as well as focusing being accomplished by rotating the hand wheels shown directly below the easel. Thus, all adjustments for scale and focus are conveniently made from a position near the easel, where the image is in full view. Enlargements up to 32 diameters are possible, with 24 × 36 mm. negatives and reductions to 1/20 the size of the original. The lens front and the negative carrier may both be tilted for special effects.

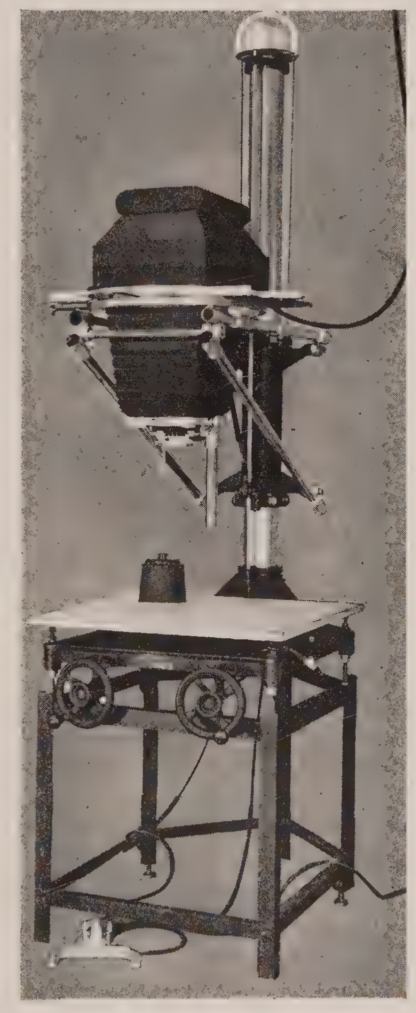

FIG. 339. Projection Printing Equipment for 8 × 10 Negatives (Saltzman).

Factors of Importance in the Selection of Projection Printing Apparatus.—In selecting projection printing apparatus, the following details should receive careful attention:

1. *Uniformity of illumination over the image at all degrees of magnification from the lowest to the highest.* The equality of illumination over the picture area may be checked by making direct readings with a photo-electric exposure meter—i.e., with the cell facing the lens—on, and at various distances from the axis or by making a flash exposure—just sufficient to produce a medium gray in the center—on a sheet of sensitized paper. Any variation in illumination will be evident as a difference in density in the flash-exposed paper.

2. *Adequate ventilation.* Ventilation is of importance to the extent to which it lessens the danger to negatives from excessive heat. In this connection, it should be noted that the important consideration is the temperature to which the negative is raised, not the temperature of the lamp house.

3. *Freedom of movement of all moving parts.*

4. *Stray light from lamp housing or around negative carrier.* This may be a source of general fogging with long exposures and is particularly objectionable when making enlarged negatives, or color separation negatives from color transparencies.

5. *Stability.* Important items in stability are freedom from vibration when adjusting to scale, focusing, or during an exposure.

6. *Quality of the projection lens.* Test for sharpness by projecting the image of a hair, fine lines cut in lead-foil, or a focusing test plate, and studying the image both in the center and at the margins of the field with a magnifier.

7. *Range of enlargement or reduction possible.*

8. *Accuracy of moving parts;* lack of "play" in focusing adjustments, negative carrier, clamp holding camera in place on upright standard, tilting lens front and other adjustments. All moving parts should be substantially constructed, conveniently placed for ease of operation in the dark.

9. *Quality of electrical equipment.* The electrical wiring and fixtures should be adequate for the purpose, well insulated and free from danger of shock and short circuits.

10. *Exposure speed;* i.e., sufficiently rapid to permit of exposures of reasonable length under all average conditions.

The Negative for Projection Printing.—Negatives for enlarging should be free from scratches, pinholes, and other physical defects.

Very thin and soft negatives are not necessary for enlarging; this being a heritage from the days when light sources were much less intense than those in general use today. Negatives without undue density in the shadow portions are desirable, however, for the photographic negative acts as a scattering medium and the scatter of light in the shadow portions of the negative is a serious obstacle to a good, rich black. Negatives for projection printing should have rather less contrast than if intended for contact printing, since the tendency in enlarging is to increase contrast.[5]

The graininess of the negative is a very important factor. Where possible, therefore, fine-grain negative material and suitable processing techniques should be employed. In enlarging from small film negatives, the granularity of the image and defects due to minute scratches and abrasions of the film base, or interference of light (Newton's rings), can be reduced by immersing the film during exposure in a liquid of approximately the same refractive index as the film base.[6] Suitable liquids for this purpose are glycerine or toluol. A small quantity of either of these is poured on a piece of clear glass and the negative laid down on the layer of liquid *so that no air bells are formed.* More glycerin or toluol is then poured on top of the negative and this covered with a sheet of glass; both sides of the film are thus covered with the liquid. In this condition, the negative is inserted in the enlarger and the exposure made. After the enlargement has been made, the film is washed for 15 minutes and dried.

The larger the degree of enlargement, the smaller is the permissible circle of confusion in the negative. If it is assumed that the smallest permissible circle of confusion is 1/100 of an inch in the enlargement, then the permissible circle of confusion in the negative will be 1/100 of an inch times the degree of enlargement. Thus, for a six times enlargement, the permissible circle of confusion would be 1/600 of an inch. For pictorial work, it is, of course, possible in many cases to have a circle of confusion in the enlargement greater than 1/100 of an inch. In most commercial work, it is doubtful if this limit may be safely exceeded, except in posters, photomurals, and other prints normally viewed from a distance.

The greater the degree of enlargement then the greater the necessity for well-corrected camera lenses, accurate focus, and precision camera and enlarger construction which will allow the definition of the lenses to be utilized to the fullest advantage.

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[5] Callier, *Phot. J.* **49** (1909) 200.

[6] Hickman, *Brit. J. Phot.* **74** (1927) 87.

Adjusting the Light Source.—When incandescent tungsten lamps are employed in reflectors, it is usually necessary to adjust the position of the lamp to secure uniform illumination only when setting up the equipment or when changing to a lamp of a different size. Once this adjustment is made, it does not need to be altered when the degree of enlargement is changed.

With condensing lenses, the position of the light must be altered if the scale of enlargement is greatly altered. The negative should first be inserted on the carrier and focused roughly to size. The carrier should then be removed and the illuminated circle examined. If the field appears darker in the center, the light source is too far from the condensers and should be moved closer; if the outer margins are uniformly darker than the center, the light source is too close and should be moved away from the condensing lenses. Colored, or dark, crescent-shaped areas on one side are due to the light source being to one side of the optical axis.

When the light source has been adjusted to produce a uniformly illuminated field, the negative carrier is re-inserted, the image focused sharply, and the exposure made.

Focusing.—Focusing presents no difficulty with an automatic focusing projection printer; the lamp-house is simply moved up or down to regulate the size of the image which remains sharp in all positions.

With equipment focused by hand, there are a number of ways of obtaining sharp focus. The negative may be inserted in the carrier and the image focused roughly to ascertain the proper size. Then insert an old negative which has been scratched with a sharp pointed instrument in the carrier and focus sharply. In some projection printers, a focusing object, consisting of two cross lines on a glass plate, is fixed on the negative carrier. If projected prints are regularly made to certain degrees of enlargement, it is a very simple matter to attach to the instrument a scale which will avoid focusing.[7]

Microscopic devices for examining the projected image to determine the position of sharp focus are available commercially.

Exposure.—The exposure may be made (1) by turning the light on and off, or (2) by means of a cap or shutter. The first method is practical only in the case of incandescent electric lamps because gaseous conductor tubes require several minutes in which to reach full intensity; with these, as with the electric arc, the exposure must be made with a shutter of some kind. A lens cap fitted with a safelight screen, or a simple flap shutter, is a decided convenience in placing the paper in position or in arranging for shading or other controls in printing.

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[7] A simple method of constructing such a scale has been outlined by Lockett, *Brit. J. Phot.* 71 (1924) 171.

The proper exposure, as in contact printing, is usually determined by means of test strips. At times, it is difficult to determine the best exposure from a test strip since so little of the image is included that it is difficult to decide what exposure produces the desired result. In such cases, a method suggested originally by Mente may be found useful. An opening is cut in a sheet of opaque cardboard, which is placed on the easel so as to expose an important part of the picture. One side of the cardboard is attached to the easel with adhesive tape. A test strip is then placed beneath the cardboard and moved between exposures in order to obtain a series of exposures of the same part of the subject on the test strip.

Another convenient method of varying the exposure in making a test strip consists in placing a scale of densities over the paper and making an exposure. The densities on the scale are such that, with an exposure of 60 seconds, different sections of the print receive exposures equivalent to 2, 3, 4, 6, 8, 12, 16, 24, 32 and 48 seconds from which the exposure producing the best result may be readily selected.

The time of exposure is the same, under the same conditions, for a contact print as for an enlargement, if the contact print is exposed in the same plane as the projected image and with the equipment set for

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Adamson—An Exposure System for Enlarging. Brit. J. Phot. **73** (1926) 475.

Dunn—Practical Method of Estimating Printing Exposures and Contrast by Densitometer. Brit. J. Phot. **84** (1937) 37.

Henderson—Finding Exposures in Bromide Enlarging. Brit. J. Phot. **62** (1915) 448.

Houskeeper—Projection Print Exposure. Phot. Tech. **1** (1939) 14.

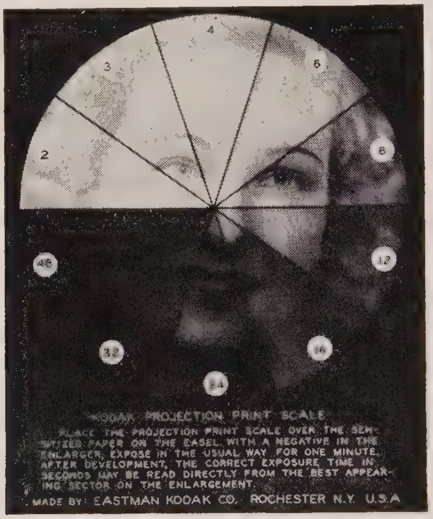
Jacobs—Exposure in Artificial Light Enlarging. Amer. Phot. **15** (1921) 490.

King—Calculation of Exposures in Enlarging. Brit. J. Phot. **53** (1906) 188.

Lockett—The Calculation of Exposures in Daylight Enlarging. Brit. J. Phot. **52** (1905) 845.

Sellors—Method of Calculating Exposures in Enlarging. Brit. J. Phot. **70** (1923) 349.

the required degree of enlargement.[8] Consequently, if the apparatus is set for an enlargement, the time of exposure may be found by placing the negative on the easel and making test exposures. The exposure producing a satisfactory contact print will be correct for the projected print, if the same paper is used.



KODAK PROJECTION PRINT SCALE
PLACE THE PROJECTION PRINT SCALE OVER THE SENSITIZED PAPER ON THE EASEL. WITH A NEGATIVE IN THE ENLARGER, EXPOSE IN THE USUAL WAY FOR ONE MINUTE. AFTER DEVELOPMENT, THE CORRECT EXPOSURE TIME IN SECONDS MAY BE READ DIRECTLY FROM THE BEST APPEARING SECTOR ON THE ENLARGEMENT.
MADE BY: EASTMAN KODAK CO. ROCHESTER N.Y. U.S.A

FIG. 340. Print Made with a Kodak Projection Print Scale Used to Determine the Proper Exposure.

Relative Exposure, Scale and Aperture in Enlarging or Reducing.—If the time of exposure under given conditions is known for one scale of enlargement or reduction, the exposure required at a different scale may be ascertained from the table on page 637.

This table is designed for use with projection printing apparatus employing diffuse illumination and is not intended for use where condensing lenses are used. The relation between the exposure and the scale of enlargement with apparatus employing condensers, depends upon a number of factors and cannot be conveniently calculated.

The exposure for a degree of enlargement not shown in the table may be determined from the following formula:

$$E = \frac{(M_2 + 1)^2 \times E_1}{(M_1 + 1)^2},$$

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[8] Lockett, *Brit. J. Phot.* **77** (1930) 743.

where E is the unknown exposure,

E_1 is the exposure under given conditions,

M_1 is the scale of enlargement for which the exposure is known,

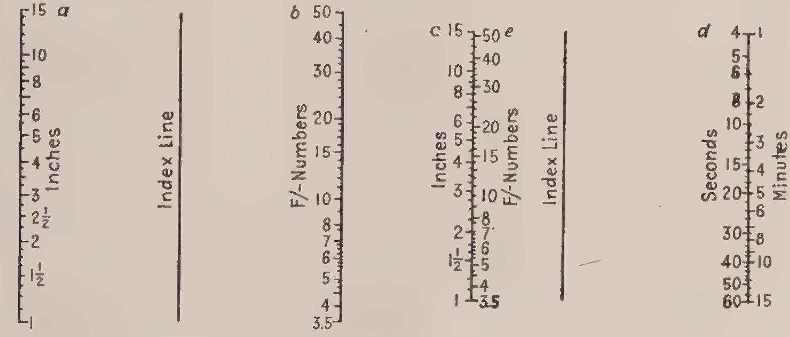
M_2 the scale of enlargement for which the proper exposure is to be found.

RELATIVE EXPOSURES WHEN ENLARGING (WITHOUT A CONDENSER)

New Times of Enlargement	*Time of enlargement for which exposure is known*											
	1	1½	2	2½	3	3½	4	5	6	8	10	12
1	1	⅔	⅖	⅓	¼	⅕	⅙	1/9	1/12	1/20	1/30	1/40
1½	1½	1	¾	½	⅖	⅓	¼	⅙	⅛	1/12	1/20	1/30
2	2¼	1½	1	¾	⅗	⅖	⅓	¼	⅕	1/9	1/12	1/20
2½	3	2	1¼	1	¾	⅗	½	⅓	¼	⅙	1/10	1/15
3	4	2½	1⅘	1¼	1	¾	⅔	⅖	⅓	⅕	⅛	1/11
3½	5	3½	2¼	1¾	1¼	1	⅘	½	⅖	¼	⅙	1/9
4	6	4	3	2	1½	1¼	1	¾	½	⅓	⅕	1/7
5	9	6	4	3	2¼	1¾	1½	1	¾	⅖	⅓	⅕
6	12	8	5	4	3	2½	2	1¼	1	⅗	⅖	2/7
8	20	13	9	7	5	4	3½	2¼	1¾	1	⅔	½
10	30	19	13	10	7	6	5	3½	2½	1½	1	¾
12	42	27	19	14	11	8	7	4½	3½	2	1½	1

To use this table find in the top horizontal line the number of times of enlargement for which exposure is known. Under this number the relative time of exposure for different degrees of enlargement will be found opposite the new times of enlargement in first vertical column.—*British Journal Almanac*

The chart which follows enables calculations involving exposure, lens aperture and scale of enlargement to be made conveniently.[9]



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[9] Collins, *Brit. J. Phot.* **70** (1923) 31.

In the general problem of exposure, there are three factors which may all vary; these are: the size of the picture, the aperture of the lens, and the duration of the exposure. Any two being known, the other can be found. The following scales provide a means of making these calculations. From Chart I is read the alteration in the *f* number required when varying the size of reproduction to obtain the same exposure. In Chart II, *C* and *D* show the mutual relation of size and exposure if the same *f* number is retained, and scales *E* and *D* connect the *f* number and the exposure when it is necessary to change either without varying the size.

To find the proper diaphragm when it is desired to alter the size of reproduction, but not the exposure, using Chart I, run the edge of a ruler from the size of the image to the aperture used. Mark the position at which the ruler cuts the index line. From this position, run the ruler to the new size of reproduction. The other end of the ruler cuts the aperture scale at the proper aperture to employ.

To determine the time of exposure with the same aperture for another degree of reproduction, scales *C* and *D* of Chart II are used. The straight edge is applied to the scales to cut scale *C* at the size of image for which the proper exposure is known and scale *D* at the time of exposure. Mark on the index line the point of intersection as before and join this point to the corresponding size of image on scale *C*. The other end of the ruler will then cut the scale *D* at the proper time of exposure for the new size of reproduction.

The aperture required for any given exposure when that for a particular is known may be calculated from scales *D* and *E*. With the edge of a ruler, join the aperture on scale *E* with the corresponding exposure on *D*. From the point of intersection with the index line, transfer the ruler so that it passes through the exposure required on scale *D*. Then the other end cuts scale *E* at the proper aperture to use.

Introducing Clouds in Projected Prints.—In the case of landscape negatives with a bald-headed sky, it is often possible to improve the pictorial effect considerably by printing in clouds from another negative. While there are several ways of doing this, the method to be described is as satisfactory as any and is perhaps the most generally useful. The image of the landscape negative is first focused on a sheet of thin cardboard placed on the easel. On this sheet of cardboard, the outline of the sky line is traced with a soft pencil. The cardboard is now removed and cut along the pencil line. The upper piece will serve to mask the sky portion while making the exposure for the landscape; the lower portion masks the landscape while the cloud is being printed.

This much done, the bromide paper is placed in position and the proper exposure given for the landscape portion, masking the sky portion by the sheet of cardboard. It is not often that the sky portion requires any masking, but when it does, the appropriate mask is held close in front of the bromide paper and kept in slight up-and-down movement with the cut-out outline in close register with the image. Now replace the orange cap on the lens and trace the outline of the sky lightly on the bromide paper with a soft lead pencil. Then, without moving the paper, the landscape negative is replaced with the cloud negative and the latter so adjusted as to secure the clouds in the desired position. Next the other mask is brought in in such a position as to cover the landscape portion and make the exposure for the clouds, keeping the mask moving up and down as before.

If the proper times of exposure for the two negatives have been accurately determined by exposing pairs of test strips and developing the two together for the same time, this procedure should result in a satisfactory effect.

Of the aesthetic factors in the combination of landscape and sky from separate negatives, it is not within the province of this work to speak. The worker's sense of the aesthetic and his knowledge of nature must ever be on guard in combination printing in order that the result be true to nature and satisfactory to the artistic sense.

Control in Projection Printing.—Much may be done to improve the print by judicious shading during the exposure. Shading may be utilized both for "holding back," i.e., making lighter, or for "printing in," i.e., making darker. The methods employed are essentially the same.

"Printing in" is accomplished by means of opaque cards with an opening of suitable size and shape held between the lens and the image. The nearer the card to the easel, the smaller the area covered and the sharper is the image. Hence, for "printing in" small areas where the light must be sharply confined, a small opening held near the image will be used. For printing in larger areas, the same opening can be used and the card moved back unless it is necessary to shade closely to a line, in which case it is better to use a larger opening nearer the image. The shape of the opening varies with that of the area to be printed in if the entire area is to be uniformly printed in Large areas, however, frequently necessitate local work requiring a smaller opening.

The shape of the opening may be altered in many cases to conform with the subject by inserting one or more fingers in the opening in such a way as to make it the desired shape.

Any portions of the image which require lightening may be held back by shading, during a part of the exposure, with a piece of cardboard or, if small, a piece of cotton attached to a small wire. This should, of course, be kept in motion during the exposure. The sharper the edge of the area to be shaded, the nearer the card should be to the sensitive paper.

Where an area with a definite edge is to be held back, or printed in, the surrounding area may be protected by a mask cut in a sheet of paper sufficiently opaque to prevent any material exposure of the sensitive paper beneath. If this mask is laid in contact with the paper, the edge must be smoothly cut and follow the outlines of the area exactly. Since this is difficult, it is better to support the mask by a sheet of good quality glass, placed several inches above the sensitive paper, so that the shadow of the mask on the sensitive paper is slightly diffused. The mask may be prepared readily by placing a light yellow non-actinic paper on the glass, sketching in the area to be printed with a lead pencil, and then cutting it out with a sharp knife.

Diffusion of the Image in Projection Printing.—It should be noted at the start that the diffusion produced by the methods about to be described, while frequently an improvement, is quite different from that produced with soft-focus lenses, or other means of producing a diffused image in the making of the negative. Diffusion introduced in the making of an enlargement is more or less general for all parts of the image, while that introduced in the original negative varies with the different planes of the subject. Moreover, when diffusion is introduced in the negative, a light halo around the highlights of the subject spreads into the adjacent shadow portions, producing an effect which corresponds more nearly to the visual impression than the reverse effect, namely, a dark halo extending into the highlight areas, which is characteristic of the diffusion introduced in projection.

There are several methods of diffusing the image in projection printing:

1. *The use of a soft-focus lens.* The amount of diffusion is controlled by the diaphragm.

2. *Diffusion disks.* Disks of ribbed glass, or perforated celluloid, for use over the lens are available commercially, usually in several series to produce different amounts of diffusion. The amount of dif-

fusion may be varied still further by making a part of the exposure with the diffusion disk and the remainder without.

Extra thin black chiffon or tulle placed in a cap over the lens produces similar results, but the time of exposure is increased and the contrast of the image reduced. White material reduces the contrast of the image to a greater degree than grey or black. One or more thicknesses may be used according to the degree of diffusion required.

3. *Diffusion screens placed near the sensitive paper.* Screens of silk bolting cloth placed in contact with, or an inch or so from, the sensitive paper are favored by many workers. The silk bolting cloth used for this purpose can be obtained from dealers in photographic supplies in a fine or medium mesh and must be kept free from creases. Wooden frames may be used for this purpose, or the cloth may be attached to a sheet of glass, using adhesive tape along the edges. When placed in contact with, or very close to, the paper, the lines show, producing a screen effect. A general softening of both definition and contrast is obtained when the screen is placed a short distance from the paper. The degree of difusion may be varied by altering the distance between the screen and the paper, or by making a part of the exposure without the screen.

Enlarging from Wet Negatives.—It is a very common practice among press photographers to enlarge from wet negatives in order to save the time required for drying. The wet film, after it has been washed briefly, is sandwiched between glasses under water, the outside of the glass is cleaned with a dry, lintless cloth, and the enlargement made. A special wet-film holder is supplied by the Eastman Kodak Company for use with the Eastman Auto-Focus Enlarger. The book-type, glassless negative carrier now common on projection printing apparatus, functions quite well with wet negatives if the metal parts do not become too hot. If there is any danger of the wet film softening from the heat, it should be placed in a 5% solution of formaldehyde for three or four minutes.

Correction of Distortion in Projection Printing.—The convergence of parallel lines—produced, for example, when tilting the camera to secure the whole of a tall building without adjusting the swing back of the camera to a vertical position—may be corrected in a measure when making a projected print. If the easel is inclined to the proper angle, the converging lines in the negative will be made parallel and the correct relationship between the width and the height of the building will be established. (The same result will be obtained if the projection apparatus is placed at an angle to the easel.) The disadvantage in this method is that a small lens aperture is usually required to get the entire image in focus. If the negative carrier is adjustable, it is possible by placing it and the easel at the proper angles to one another, to correct converging lines in the subject without having to use a small lens aperture to secure sharp focus over the whole of the image.

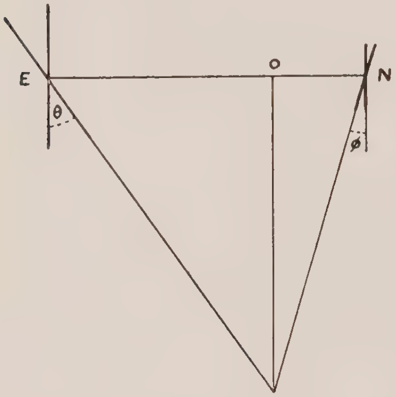

FIG. 341. Illustrating the Relative Angles of Inclination of the Paper and the Negative when Inclined for the Correction of Distortion.

In Fig. 341, the easel and the negative are inclined through the angles θ and ϕ. The geometrical condition necessary for sharp focus over the image is that the planes of both easel and negative meet in a plane drawn through the optical center of the lens and prependicular to its optical axis. Thus $\tan \theta = m \tan \phi$, OE being m times ON, m thus being the scale of enlargement. In other words, the angular inclination of the easel is equal to that of the negative multiplied by the scale of enlargement. In practice, matters are simplified by first inclining the easel until converging lines are approximately parallel, and then inclining the negative until the image is sharp.

However, if both negative and easel are inclined to permit the use of the lens at a large relative aperture, the height of the building, or other object, is reduced. In other words, the distance between the vertical lines which have been made parallel is relatively greater than their height. The vertical dimension of the image is therefore compressed in the process. Very often, this is so slight as to be of no real importance. At other times, it may even be an advantage. In some cases, however, it is objectionable. When this is found to be true, the simplest procedure, when it can be done, is to incline only the easel. With a lens of the proper focal length, it is possible to incline both the negative and the easel without compressing the image in either dimension. The focal length of the lens required depends upon the degree of enlargement and the angular inclination necessary to render converging lines parallel.

The distortion produced by inclining the easel and/or the negative, may be used also to alter the proportions of the image as, for example, to increase the height of a tree, a building, or a standing figure. The elongated figures demanded for fashion illustration may be produced in this manner. Grotesque effects are produced if the process is carried to extremes; a small amount of such distortion, however, in some cases adds to the effectiveness of the picture.

BURCHALL—Rectification without Enlargement. Brit. J. Phot. **82** (1935) 741.

CHARLES—Can Converging Verticals be Made Correct? Brit. J. Phot. **84** (1937) 243.

GRANGER—An Easy Practical Method of Rectifying Converging Perpendiculars in Architectural Subjects. American Annual of Photography **51** (1937) 220.

ROBINSON—Distortion in Correcting Verticals. Brit. J. Phot. **84** (1937) 343.

WRIGHT—Correcting Verticals by Enlargement. Brit. J. Phot. **83** (1936) 431.

SMETHURST—Enlarging Exposure Factors Required with an Opal Lamp and Condenser as Illuminant. Brit. J. Phot. **85** (1938) 483; Exposure Factors in Projection Printing with Condenser. Ibid.

DUNN—Factors in Enlarging. Brit. J. Phot. **85** (1938) 99, 115.

LEE—Rectification of A Negative Made on An Inclined Plate. Phot. J. **82** (1942) 74.

CHAPTER XXIV

TONING OF DEVELOPED SILVER IMAGES

Introduction.—The process by which the color of a print, or transparency, is changed through the replacement of the silver image with one consisting of a metallic compound or a dye is known as toning. Compounds of sulfur, iron, copper, lead, gold, uranium, tin, selenium vanadium and cobalt are used but the first mentioned is by far the most important. Dye toning processes are reserved almost exclusively for transparencies. Representative formulae and instructions for toning with these substances will be given in this chapter; for additional information on toning, reference should be made to the bibliography.

Sulfur Processes—The Print.—The color obtained upon toning depends in part upon the process but more particularly upon the emulsion and the exposure and development of the black and white image.

The smaller the average grain size of the developed image the warmer or more yellowish the color of the image after toning. Chlorobromide and chloride papers tend to produce warmer tones than those coated with an emulsion of silver bromide.

Although numerous statements to the contrary may be found in the literature, the particular developing agent employed has little effect on the color of the toned image. Development in solutions heavily restrained with a soluble bromide, however, result in warmer, i.e., more yellowish, colors, due to the finer grain of the reduced silver deposit.

The time of development is, with any particular paper and developing solution, a very important factor in determining the color of the toned image. Shortening the time of development results in warmer colors; lengthened development in colder, more purplish tones; the limit being reached upon development to finality.

Developing Time
Less Greater
warmer colors ←————|————→ colder colors

Particle Size
Small ←————|————→ Large

With a given time, or degree of development, exposure is without effect on the color of the toned image and controls the depth or intensity only.

In practice, therefore, the color of the image with any particular paper and developer may be controlled within certain limits, by variation (1) of the amount of soluble bromide in the developer and (2) the time of development.

When developing for a fixed time, the developer should be renewed frequently or the accumulated bromides and restraining by-products of the reaction will affect the color of the image when toned. The variation in color due to differences in the composition of the developer and the time of development is more marked in the toned than in the black image.

Prints intended for toning should be slightly darker than those to be left in their original state in order to allow for the reduction in depth which occurs in toning.

Hypo-Alum Process of Sulfur Toning.—The hypo-alum toning bath is prepared by dissolving ordinary alum (potassium aluminum sulfate) in a hot solution of hypo.

The reactions taking place when toning in a solution of hypo and alum may be represented as follows:[1, 2]

$$Al_2(SO_4)_3 + 3Na_2S_2O_3 = Al_2(S_2O_3)_3 + 3Na_2SO_4,$$
$$Al_2(S_2O_3)_3 + 3H_2O = Al_2(OH)_3 + 3SO_2 + 3S,$$

or

$$Al_2(SO_4)_3 + 3H_2O = Al_2(OH)_3 + 3H_2SO_4,$$
$$Na_2S_2O_3 + H_2SO_4 = Na_2SO_3 + SO_2 + S,$$

and

$$Ag_2 + S = Ag_2S.$$

A bath consisting of hypo and alum alone has a solvent action on finely divided silver causing the image to be bleached in the process of toning, hence the bath is first "ripened" through the addition of silver either as silver nitrate or by toning waste prints.

The following forms a satisfactory hypo-alum toning bath.

Cold water	2800.0 cc.	90 oz.
Sodium Thiosulfate (Hypo)	480.0 gm.	16 oz.

[1] Seyewetz and Chicandard, *Eder's Jahrbuch* **10** (1896) 488.

[2] Sheppard, *Photography as a Scientific Implement*, p. 167.

NITZE—Paper, Developer and Bleach in Sulphide Toning. Brit. J. Phot. **79** (1932) 486–487.

Dissolve thoroughly, then add the following solution:

Hot water (about 160° F.) (71° C.)	640.0 cc.	20 oz.
Potassium Alum (E. K. Co.)	120.0 gm.	4 oz.

Then add the following solution (including precipitate) slowly to the above hypo-alum solution while stirring the latter rapidly.[3]

Cold water	64.0 cc.	2 oz.
Silver Nitrate (Crystals) (E. K. Co.)	4.2 gm.	60 gr.
Sodium Chloride (Table salt)	4.2 gm.	60 gr.
After combining above solutions, add water to make	4.0 liters	1 gal.

Note: *The silver nitrate should be dissolved completely before adding the sodium chloride, and immediately afterwards the solution, including the milky white precipitate, should be added to the hypo-alum solution as directed.*

For use, pour into a tray standing in a water bath and heat the toning bath to 120° F. (49° C.). Never use the bath if the temperature is above 120° F. (49° C.) or blisters and stains will result. Prints will tone in 12 to 15 minutes depending upon the grade of paper. Toning should not be continued longer than 20 minutes at 120° F. (49° C.).

The formation of a black or gray precipitate in the bath in no way impairs the toning action of the bath if proper manipulation technic is used.

Prints should be immersed thoroughly and separated occasionally, especially during the first few minutes, to insure even toning. The black prints should be a shade dark and developed from 1½ to 2 minutes without forcing, to produce good sepia tones. After prints are toned, sponge off any sediment in warm water and wash for one hour in running water. Dry prints should be soaked thoroughly in water before toning.

The time required for toning may be reduced by placing the fixed and washed prints in a 10% solution of sulfuric acid (commercial) for one minute and then transferring directly to the toning bath.[4] Toning then proceeds rapidly.

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[3] The addition of ammonia, sodium phosphate or potassium iodide is sometimes recommended. Ammonia: *Brit. J. Phot.* **68** (1921) 773; **70** (1923) 570. Sodium phosphate: *Brit. J. Phot.* **51** (1904) 1022. Potassium iodide: *Brit. J. Phot.* **67** (1920) 437.

[4] *Brit. J. Phot.* **69** (1922) 126.

The addition of gold chloride results in darker and colder (more purplish) colors. The toned image in this case consists of gold sulfide and silver sulfide, the latter predominating.

The following is a satisfactory formula for a hypo-alum-gold toning bath:

Solution No. 1

Warm water (about 125° F.) (52° C.)	4.0 liters	1 gal.
Sodium Thiosulfate (Hypo)	960.0 gm.	2 lb.
Ammonium Persulfate	120.0 gm.	4 oz.

Dissolve the hypo completely before adding the ammonium persulfate. Stir the bath vigorously while adding the ammonium persulfate. If the bath does not turn milky, increase the temperature until it does.

Prepare the following solution and add it, including precipitate, slowly to the hypo-persulfate solution while stirring the latter rapidly. *The bath must be cool when these solutions are combined.*

Cold water	64.0 cc.	2 oz.
Silver Nitrate (Crystals) (E. K. Co.)	5.2 gm.	75 gr.
Sodium Chloride (Table salt)	5.2 gm.	75 gr.

Note: *The silver nitrate should be dissolved completely before adding the sodium chloride.*

Stock Solution No. 2

Water	250.0 cc.	8 oz.
Gold Chloride	1.0 gm.	15 gr.

For use, add 4 ounces (125 cc.) of solution No. 2 slowly to solution No. 1 while stirring the latter rapidly. The bath should not be used until it has become cold and has formed a sediment. Then pour off the clear liquid for use. Pour the clear solution into a tray standing in a water bath and heat to 110° F. (43° C.). The temperature, when toning, should be between 100° and 110° F. (38° and 43° C.). Dry prints should be soaked thoroughly in water before toning.

Keep at hand a black-and-white print for comparison during toning. Prints should be separated at all times to insure even toning. When the desired tone is obtained, rinse the prints in cold water. After all have been toned, return them to the fixing bath for five-minutes, then wash for one hour in running water.

The bath should be revived at intervals by the addition of gold solution No. 2. The quantity to be added will depend upon the number of prints toned and the time of toning. For example, when toning to a warm brown, add 1 dram (4 cc.) of gold solution after each fifty 8 × 10 inch prints or their equivalent per gallon (4 liters) have been toned. Fresh solution may be added from time to time to keep the bath up to the proper volume.

Sulfur Toning with Acid Hypo.—When an acid is added to a solution of hypo, the latter is decomposed, one of the products of the reaction being finely divided sulfur. This reacts with the metallic silver of the image to form silver sulfide. A number of toning processes based upon this principle have been published. They are however but little used.[5] Toning is not completed within the bath itself but only after washing for thirty minutes to one hour to allow sufficient time for the colloidal sulfur to react with the silver image.[6]

Sulfur Toning with the Polysulfides.—A cheap and simple method of sulfur toning and one which produces acceptable results on many emulsions consists in the use of a polysulfide, or the inexpensive liver of sulfur, a mixture of potassium sulfide and potassium sulfate which usually contains impurities in the form of potassium carbonate and potassium hyposulfite.

The action of the polysulfide on finely divided metallic silver is probably as follows:[7]

$$S + H_2O \rightarrow H_2S + O,$$
$$Ag_2 + \rightarrow Ag_2O,$$
$$Ag_2O + H_2S \rightarrow Ag_2S + H_2O.$$

Using liver of sulfur the following formula is satisfactory:

Liver of sulfur	125 gm.	¼ oz.
Hypo	25 gm.	½ oz.
Water to	1000 cc.	20 oz.

Use at a temperature from 80° to 90° F. (27° to 32° C.). Toning requires from 10 to 15 minutes but the final color becomes apparent only upon washing for several minutes.

Since the actual toning agent is the polysulfide contained in the liver of sulfur it is plain that this may be used. It may be prepared by dissolving pure sulfur in commercial ammonium sulfide until a saturated solution is produced and then withdrawing the clear solution for use. For toning, from 10 to 15 drops are added to 10 ounces of water (2 cc. to 1000 cc.) and heated to a temperature of 85° to 90° F. (30° to 32° C.). Toning proceeds rapidly and is usually complete in 10 to 15 minutes.[8]

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[5] Lumière, A. and L. and Seyewetz, *Brit. J. Phot.* **59** (1912) 972. Soar, *Brit. J. Phot.* **60** (1913) 156, 185. Hoell, Eastman Research Laboratory, *Brit. J. Phot.* **69** (1922) 73. Meuser, *Phot. Ind.* (1916) 19; *Eder's Jahrbuch* **29** (1915) 408.

[6] Rawling, *Phot. J.* **62** (1922) 3.

[7] Lumière, A. and L. and Seyewetz, *Brit. J. Phot.* **70** (1923) 733.

The addition of 2% of potassium thiocyanate increases the rate of toning but has little effect on the color, which however tends to purple.[9]

Direct Sulfiding Baths Employing an Oxidizing Agent.—Processes of this type depend upon the use of an oxidizing agent which converts the silver image into a salt which is immediately attacked by the sulfiding agent and converted into silver sulfides.

A number of agents have been employed for this purpose, among them ammonium thiocyanate,[10] potassium ferricyanide alone and in conjunction with potassium bromide [11] and nitrobenzene.[12]

The following formula utilizing ammonium thiocyanate produces on many papers a tone similar to that obtained by gold toning of print-out papers:

A.	Ammonium thiocyanate	455 gm.	8 oz.
	Water to	1000 cc.	16 oz.
B.	Sodium sulfide	152 gm.	2⅔ oz.
	Water to	1000 cc.	16 oz.

The toning solution is prepared by mixing *directly before use*

A	8 parts
Water	24 parts
B	1 part

Toning requires from 15 to 40 minutes at a temperature of 70° to 80° F. (21° to 27° C.) or 5 to 15 minutes at 90° to 100° F. (33° to 38° C.). A higher temperature is not advisable owing to the action of the sulfocyanide on the gelatin.

Using nitrobenzene a suitable formula is: [13]

Barium sulfide (saturated solution)	15 parts
Sodium meta-nitrobenzene sulfonate (10% solution)	1 part

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[8] Underberg, *Brit. J. Phot.* **71** (1924) 50.

[9] Bullock, *Brit. J. Phot.* **68** (1921) 450.

[10] Punnett, *Brit. J. Phot.* **56** (1909) 571. Potassium persulfate. Kropf, *Brit. J. Phot.* **57** (1910) 837.

[11] Triepel, *Brit. J. Phot.* **58** (1911) 657. Mente, *Eder's Jahrbuch* **26** (1912) 507. Blake-Smith, *Brit. J. Phot.* **57** (1910) 520.

[12] Shaw, *Brit. J. Phot.* **70** (1923) 267, 591.

[13] Shaw, *Brit. J. Phot.* **70** (1923) 759.

Prints immersed in this solution tone to a good sepia within 3 to 5 minutes at a temperature of 60° F. (16° C.). The color varies greatly, however, with the paper.

The reaction taking place, according to Sheppard,[14] is as follows:

$$C_6H_5NO_2 + 4Ag + 2NaSH = C_6H_5.NH.ONa + NaOH + 2Ag_2S.$$

Indirect Processes of Sulfur Toning.—In the indirect process of sulfur toning the fixed and washed prints are first bleached in a solution of an oxidizing agent which converts the silver of the image into a compound which is capable of being converted into silver sulfide when the print is placed in a suitable sulfiding bath.

The color obtained with the indirect method of sulfur toning tends to be more yellowish than that produced by the direct processes which are on this account the more generally suitable for chloride papers. The indirect process, however, is especially well adapted to bromide papers which in many cases tend to produce a cold and rather purplish color when toned in the hypo-alum bath or by one of the other processes of direct sulfur toning. As with the other processes the color obtained depends primarily upon the paper and exposure and development of the print rather than on toning, although certain changes in the procedure (to be noticed later) do influence the final color.

Prints for toning by the indirect process should be thoroughly fixed and washed. Incomplete fixation results in discoloration of the whites from the conversion of the silver salts left in the print into silver sulfide.[15]

Thorough washing is essential since traces of hypo remaining in the print combine with the oxidizing agents used in the bleacher forming a reducer.

The commonest bleaching solution consists of potassium ferricyanide and potassium bromide; however, many other oxidizing agents may

[14] *Brit. J. Phot.* **70** (1923) 679.

[15] Lumière and Seyewetz, *Brit. J. Phot.* **70** (1923) 732.

Backstrom and Bostrom—The Influence of the Bleaching Bath on the Colour Obtained in the Indirect Sulphide-Toning Process. Phot. J. **76** (1936) 607.

Jelley—A Cause of Yellowness in Sepia Toning. Phot. J. **72** (1932) 480–485.

Morris—Stains in Sulphide Toning. Brit. J. Phot. **80** (1933) 127.

Wiegleb—Methods of Sulphite Toning. Brit. J. Phot. **76** (1929) 344–346, 363–365, 375–377.

be used, namely, potassium or ammonium bichromate,[16] chromic acid, potassium permanganate,[17] ammonium persulfate, hypochlorite, and quinone.[18]

The reactions which take place in the case of a bleaching bath composed of potassium ferricyanide and bromide are probably as follows:

Bleaching

$$(1)\ 4Ag + 4K_3Fe(CN)_6 = 3K_4Fe(CN)_6 + Ag_4Fe(CN)_6,$$

$$(2)\ Ag_4Fe(CN)_6 + 4KBr = K_4Fe(CN)_6 + 4AgBr.$$

Sulfiding

$$2AgBr + Na_2S = Ag_2S + 2NaBr.$$[19]

Slight, but relatively unimportant, differences in the color of the toned image result from variations in the composition of the bleaching solution.[20] Bleaching baths containing a bichromate are not widely used because of the time required in washing but the color apparently varies less with differences in exposure and development than when the more familiar ferricyanide-bromide bleacher is used. A solution of potassium ferricyanide alone results in a more yellowish color than when the bleaching solution contains bromide. With a ratio of 3:1 for the ferricyanide and bromide, increasing the concentration of the former above 3% tends to yellowness. The substitution of a chloride for bromide also results in more yellowish colors. Substituting 0.1% of potassium thiocyanate for the bromide results, with some papers, in a purplish color and slight reduction of the image.[21]

The following is a suitable formula for the bleaching solution:

Ammonium bromide	11 gm.	85 gr.
or Potassium bromide	13 gm.	98 gr.
Potassium ferricyanide	35 gm.	270 gr.
Water to make	1000 cc.	16 oz.

The addition of sodium carbonate avoids yellowish colors.

Potassium bromide	15 gm.	65.6 gr.
Potassium ferricyanide	35 gm.	153.0 gr.
Sodium carbonate (des.)	7.5 gm.	32.8 gr.
Water to make	1000 cc.	10.0 oz.

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[16] *Brit. J. Phot.* **56** (1909) 233; **64** (1917) 173.

[17] *Brit. J. Phot.* **63** (1916) 659; **62** (1915) 353.

[18] Lumière and Seyewetz, *Bull. Soc. franç. Phot.* **62** (1920) 267.

[19] Carnegie, *Brit. J. Phot.* **53** (1906) 219, 947. Jelley, *Phot. J.* 72 (1932) 480.

[20] Bullock, *Brit. J. Phot.* **68** (1921) 447.

[21] Bullock, *Brit. J. Phot.* **68** (1921) 447.

Sulfiding.—Sodium sulfide is generally used for this purpose although sulfur and other sulfur compounds may be used, namely, the corresponding barium and ammonium sulfides,[22] sodium sulfantiomoniate ($Na_3SbS_4.9H_2O$),[23] sulfoxyphosphates such as Na_2SPO_3,[24] sodium sulfoxalate formaldehyde, $NaHSO_2.CH_2O.2H_2O$,[25] and thiomolybdates, thiotungstates, thiostannates and similar thio compounds.[26]

Only pure sodium sulfide should be used and it should be fresh as it oxidizes readily forming caustic soda and hypo. The weakening of the sulfiding bath resulting from the use of impure sodium sulfide, an oxidized solution, or the presence of hypo results in yellowish tones. The caustic soda leads to softening of the gelatin and is a source of blisters.

Sodium sulfide	1 gm.	8 gr.
Hydrochloric acid	1 gm.	8 gr.
Water to	1000 cc.	16 oz.

The odor of the barium salt is less objectionable than that of sodium sulfide, but insoluble carbonates and sulfates of barium are precipitated in the gelatin unless distilled water is used. The use of sodium sulfantimoniate (Schlippe's salt) results in an image consisting probably of some antimony sulfide as well as silver sulfide and colors ranging from an orange-red to much colder colors by the addition of ammonia.[27]

A tendency towards yellowish brown tones noticeable on certain papers (warm tone) may be avoided by placing the bleached and well washed prints for 15 to 20 seconds in a 1% solution of sodium carbonate, rinsing and then sulfiding.[28, 29]

Another method, involving partial redevelopment of the image combined with sulfiding, consists in the use of a pyrocatechin developer with the addition of sodium sulfantimoniate ($Na_2SbS_4.9H_2O$). The bleached and well washed prints are redeveloped in:

A.	Pyrocatechin	20 gm.	155 gr.
	Sodium sulfite (des.)	50 gm.	385 gr.
	Water to make	1000 cc.	16 oz.
B.	Sodium carbonate (des.)	85 gm.	650 gr.
	Water to make	1000 cc.	16 oz.

[22] Namias, *Brit. J. Phot.* **58** (1911) 324. *Brit. J. Phot.* **54** (1907) 523.

[23] Blake-Smith, *Phot.* **12** (1904) 30.

[24] Lumière, F.P. 507,332: *Sci. et Ind. Phot.* Series I, **I** (1921) 4.

[25] Miller, *Phot. Ind.* (1925) 1064.

[26] Smith, *Phot. J.* **48** (1908) 267.

[27] Sedlaczek, *Brit. J. Phot.* **53** (1906) 624, 645.

[28] Jelley, *Phot. J.* **72** (1932) 480.

[29] Bullock, *Brit. J. Phot.* **68** (1921) 447.

For use take 1 part *A* to 2 parts of *B* and add from 2 to 5% of a 10% solution of sodium sulfantimoniate. The color of the image may be regulated by varying the amount of sulfantimoniate in the redeveloper. Colors from red-chalk to a good sepia are obtainable on most papers.[30]

Gold Toning.—Gold toning has become quite popular in recent years and is certainly effective for subjects for which a cold blue or purplish-blue color is suitable.

The following is a good formula:[31]

A.	Gold chloride	1 gm.	10 gr.
	Water to make	300 cc.	6 oz.
B.	Thiocarbamide	1.6 gm.	15 gr.
	Water to make	300 cc.	6 oz.
C.	Citric acid	7.5 gm.	65 gr.
	Water to make	300 cc.	6 oz.

For use take:

A	1 part
Water	3 "
B	1 "
Water	3 "
C	1 "
Water	3 "

Finally mix the three solutions.

Gold Toning of Sulfided Prints.—Red colored images may be obtained by gold toning of the sulfide toned print. The gold toning bath is prepared as above. The sulfided and washed prints are placed in this bath and kept in motion to prevent uneven action. Toning requires from 15 to 25 minutes depending upon the paper and the color desired. The brown color of the sulfur toned print first assumes a reddish color and gradually approaches a pure red.

After toning the prints are washed for 2 to 3 minutes and fixed for 5 minutes in a fresh acid fixing bath, then well washed and dried.[32]

The gold toned image appears to consist of a double sulfide of silver and gold.[33]

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[30] Valenta, *Phot. Korr.* **49** (1912) 279.

[31] Wiegleb, *Brit. J. Phot.* **76** (1929) 377.

[32] With developed silver images the above gold toning bath produces a blue-black deposit. Gold toning may be beneficial in such cases if the original print is slightly muddy or greenish in color.

[33] Lumière and Seyewetz, *Brit. J. Phot.* **70** (1923) 331.

Reduction of Sulfide Toned Images.—If the print is too dark after toning it may be reduced by placing it for a few seconds in[34]

Cupric bromide	30 gm.	230 gr.
Sodium chloride (salt)	250 gm.	4½ oz.
Water to make	1000 cc.	16 oz.

Toning with Stannous (Tin) Salts.—Processes of toning employing tin salts are of greater interest theoretically than practically. Unlike other toning processes in which the silver of the image is replaced or converted into a chemical compound, in the case of tin salts an adsorption compound of colloid silver is formed.

If stannous chloride is employed the following reaction may be regarded as taking place.[35]

$$\mathrm{Sn} + 4\mathrm{OH} = \mathrm{SnO_2} + \mathrm{H_2O},$$
$$2\mathrm{Ag} + \mathrm{SnO_2} = 2\mathrm{Ag} + \mathrm{SnO_2}.$$

The prints are first bleached in a solution of ferricyanide and bromide, or copper chloride. The bleaching formula for sulfide toning (p. 651) is suitable.

The prints are then washed thoroughly and placed in a solution of sodium stannite prepared as follows:[36]

Stannous chloride	10 gm.
Water to	100 cc.

To this add with constant shaking 70 cc. of a 10% solution of caustic soda until the precipitate first formed is redissolved. Finally add

Water	80 cc.

This results in a purplish black color on bromide prints and a sepia-brown with chloride developing papers. Warmer colors may be obtained by using potassium stannite which is prepared in a similar manner using, however, 100 cc. of a 10% solution of potassium hydroxide and 50 cc. of water to each 100 cc. of a 10% solution of stannous chloride.[37]

Toning with Hydrosulfite.—Pleasing warm brown, purple brown and sepia tones are obtainable on many papers with an acid solution of sodium hydrosulfite. The formula follows:

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[34] Smith, *Phot. J.* **47** (1907) 281.

[35] Formstecher, *Brit. J. Phot.* **68** (1921) 759.

[36] Formstecher, *Brit. J. Phot.* **68** (1921) 759.

[37] References on toning with tin. Gamble and Woolley, *Brit. J. Phot.* **60** (1913) 978. Formstecher, *Brit. J. Phot.* **68** (1921) 759. Druce, *Brit. J. Phot.* **69** (1922) 433.

Sodium hydrosulfite ($Na_2S_2O_4$)	2 gm.	56.0 gr.
Oxalic acid (5% sol.)	25 cc.	1 oz. 5 dr.
Water to	150 cc.	10.0 oz.

Toning requires from 20 to 40 minutes at a temperature of 65°. The odor produced by the decomposition of the hydrosulfite is decidedly unpleasant.

Toning Processes Employing Selenium.—Selenium is similar chemically to sulfur and both the alkali selenides and the acid compounds have been employed for toning alone and in combination with hydrosulfite.[38]

The following is one of the many formulas which have been patented:[39]

Sodium sulfide (20% sol.)	500 cc.	10 oz.
Red amorphous selenium	0.5 gm.	4.5 gr.

The selenium is added to the solution of sodium sulfide, stirred briskly, and left to stand for several hours at room temperature. The filtered solution produces purple brown and reddish brown colors depending upon the character of the paper.

The following formula[40] is recommended for chloro-bromide papers on which colors ranging from a bluish-purple to red-brown are obtainable, depending largely upon the time of immersion:

Sodium sulfite (des.)	150 gm.	12 oz.
Selenium powder	6 gm.	210 gr.
Ammonium chloride	190 gm.	15 oz.
Water to make	1000 cc.	80 oz.

To prepare, dissolve the sulfite in about three-fourths of the total quantity of hot water, add the selenium powder and boil until it is dissolved. Allow the solution to cool, then add the ammonium chloride

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[38] For a comprehensive survey of the subject see: Sedlaczek, *Brit. J. Phot.* **5** (1928); **76** (1929) 6.

[39] G.P. 301,019 by Mimosa, A. G.

[40] Twinn, *Phot. J.* **85** (1938) 485.

Asloglou—Selenium Toning Methods for Prints. Brit. J. Phot. **85** (1938) 599, 629, 643, 662.

Formstecher—History and Theory of Selenium Toning. Phot. Ind. **34** (1936) 1014.

Milbauer—Selenium Toning. Phot. Korr. **65** (1929) 10–12, 45–47.

Trevelyan—Commonsense Toning. J. Phot. Soc. Amer. **7** (1941) 149.

and stir until dissolved. Finally, dilute with cold water to the proper volume.

For use, dilute one volume of the stock solution with five of water.

Prints should be well washed and preferably dried before toning. The toning solution is used at normal room temperature—65° to 70° F. (18° to 21° C.), and the time of toning varies from 5 to 15 minutes, depending upon the paper and the color desired. Only chlorobromide papers produce rich, warm colors; very little toning action is apparent on bromide or chloride papers.

Mercury-Sulfide Toning.—The addition of mercuric chloride to a bleaching solution of potassium ferricyanide and bromide followed by sulfiding in the usual manner results in an image consisting partly of silver sulfide and partly of a mercuric compound. The colors obtained range from a normal sepia to a warm engraving black depending upon the relative proportions of the mercury compound and silver sulfide. The bleaching solution is prepared as two stock solutions:

A.	Potassium ferricyanide	100	gm.	1	oz.
	Potassium bromide	150	gm.	1½	oz.
	Water to make	1000	cc.	9	oz.
B.	Mercuric chloride	12.5	gm.	60	gr.
	Potassium bromide	12.5	gm.	60	gr.
	Water to make	500	cc.	5	oz.
C.	Sodium sulfide	100	gm.	1	oz.
	Water to make	1000	cc.	9	oz.

Color	*A*	*B*	Water	Rel. Exposure
Normal sepia	40 parts	— parts	480 parts	10 sec.
Cool sepia	40 "	20 "	480 "	9 "
Colder sepia	30 "	30 "	480 "	8 "
Brown-black	30 "	50 "	480 "	7 "
Engraving black	30 "	90 "	480 "	6 "

After having been bleached in a bleacher compounded as directed for the tone desired, the prints are washed briefly and passed through three successive baths of 1% hydrochloric acid after which they are again washed and finally sulfided as usual.[41]

Copper Toning.—The range of colors obtainable with copper toning extends from warm black through various shades of brown to red chalk, the various colors following one another in a definite order as the action proceeds. The chemical reactions taking place are probably as follows:

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[41] Bennett, *Brit. J. Phot.* **68** (1921) 25.

$$CuSO_4 + 2KBr = CuBr_2 + K_2SO_4,$$
$$CuBr_2 + Ag = CuBr + AgBr,$$
$$CuBr + 2AgNO_3 = Cu(NO_3)_2 + Ag_2Br.$$

The following is a satisfactory formula. Two solutions are required as follows:[42]

A.	Cupric sulfate	6.25 gm.		60 gr.
	Potassium citrate (neutral)	25	gm.	240 gr.
	Water to make	1000	cc.	20 oz.
B.	Potassium ferricyanide	5.2	gm.	50 gr.
	Potassium citrate	25	gm.	240 gr.
	Water to make	1000	cc.	20 oz.

For use take equal parts. Should the prints appear purplish in the highlights increase the amount of potassium citrate in either *A* or *B*.[43]

Uranium Toning.—The range of tones obtainable by toning with uranium extends from warm-black, through various shades of brown to plum colors and various shades of red, terminating in a bright brick-red. The toning action is progressive, the various colors appearing in a definite order as the action is allowed to proceed.

As the image is intensified in the process of toning, the black and white print should be lighter than normal.

The chemical reactions occurring are probably as follows:

$$8Ag + 4(UO_2)_3[Fe(CN_6)]_2 = 2Ag_4Fe(CN)_6 + 3(UO_2)_4[Fe(CN_6)]_2.$$

Prints intended for toning in uranium should be thoroughly washed as the presence of hypo results in stain which cannot be removed.

The following formula is suitable:[44]

Uranyl nitrate	5	gm.	38 gr.
Potassium citrate	5	gm.	38 gr.
Potassium ferricyanide	2	gm.	15 gr.
Ammonia alum	10	gm.	77 gr.
Pure hydrochloric acid	0.3	cc.	2 min.
Water	1000	cc.	16 oz.

[42] British Journal Formula.

[43] Other methods of toning with copper: Namias, *Bull. Soc. franç. Phot.* **64** (1922) 26.

[44] Ferguson, *Phot. J.* **25** (1900) 113. Sedlaczek, *Phot. Ind.* (1924) 234. *American Photography* **19** (1925) 8.

A print immersed in the above toning solution shows no change for about a minute, after which a slight brownish color becomes apparent. This gradually changes into reddish brown as the action proceeds. When toning has proceeded to the point desired, the print is washed for 1 to 2 minutes and placed in:

Potassium citrate	5 gm.	38 gr.
Sodium sulfate (not sulfite)	25 gm.	192 gr.
Water	1000 cc.	16 oz.

Three or four such baths may be required to remove the yellowish coloration entirely. The print should then be washed in running water free from alkalis for a minute or so, then fixed for 5 minutes in a 0.5% solution of hypo followed by washing in running water made acid by the addition of 0.1% of glacial acetic acid.

Toning with Vanadium.—The following is a suitable formula:

Vanadium oxalate solution (20%)	50 cc.	½ fl. oz.
Oxalic acid (saturated solution)	50 cc.	½ fl. oz.
Ammonia alum (saturated solution)	50 cc.	½ fl. oz.
Ferric oxalate solution	quant. suff.	
Glycerin	50 cc.	½ fl. oz.
Potassium ferricyanide solution (10%)	10 cc.	48 min.
Water	1000 cc.	10 oz.

Toning requires from 10 to 15 minutes, after which the prints are immersed in a 10% solution of sodium sulfate for 5 minutes, washed several minutes and dried. Fixing is unnecessary.

The result of toning in the above solution is to produce an image consisting partly of blue ferri-ferrocyanide and partly of yellow vanadium ferrocyanide, the two combining to produce a green. The only practical application of vanadium as a toning agent is for the purpose of producing green colored images.

Dye Toning.—The range of colors obtainable by toning with metallic compounds is rather limited; a much broader range is possible by dye toning. Dye toning should not be confused with tinting or staining. A dye toned image consists of a colored dye image in uncolored gelatin; in a tinted image the gelatin is more or less uniformly stained by the dye.

To produce the preferential deposition of the dye so as to form a dye image, it is necessary to convert the silver image into an inorganic compound which will cause the dye to come out of solution and precipitate on the compound. Such a substance is called a *mordant* and the dye is said to be mordanted. Silver ferrocyanide is a typical mordant.

Consequently if a silver image is converted into an image of silver ferrocyanide and immersed in a solution of a basic dye, the dye is precipitated upon the silver ferrocyanide producing a mordanted dye image.[45]

A comparatively large number of inorganic compounds have been used as mordants; among them silver iodide,[46] various ferrocyanides[47] and sulfocyanides,[48] silver sulfide,[49] lead[50] and iron.[51]

Dye toning is reserved more particularly for transparencies although methods involving the application of the dye solution by brushes or cotton to the surface of prints on paper have been described.[52]

Silver ferrocyanide is one of the best mordants for basic dyes and the following is a satisfactory formula:[53]

Uranium Mordanting Bath.—

Uranium (uranyl) nitrate..............	8.0 gm.	8 lb.	114 gr.
Oxalic acid.........................	4.0 gm.	4 lb.	57 gr.
Potassium ferricyanide................	4.0 gm.	4 lb.	57 gr.
Water to make......................	1.0 liter	120 gal.	32 oz.

Directions for Mixing. The uranyl nitrate should be of good quality and should not contain an excess of free nitric acid. First dissolve each chemical separately in a small volume of water. Then add the oxalic acid solution to the uranyl nitrate solution and finally add the ferricyanide solution. If the uranyl nitrate is added directly to the potassium ferricyanide, a brown precipitate will be obtained which will not dissolve readily in the oxalic acid. After mixing, the bath should be light yellow and perfectly clear. The solution should not be exposed to light any more than necessary.

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[45] The theory of the mordanting of dyes as applied to dye toning is as yet incomplete. In general, however, the process appears to involve the mutual precipitation of oppositely charged colloids. Bullock, *Brit. J. Phot.* **70** (1923) 352; *Amer. Phot.* **17** (1923) 756.

[46] Traube, D.R.P. 187,289 of 1905, *Brit. J. Phot.* **53** (1906) 942.

[47] Clark, *Scientific Publications Eastman Research Laboratories,* **2** (1915) 130. Traube, B.P. 147,005 of 1916, *Brit. J. Phot.* **68** (1921) 328. Crabtree, U.S.P. 1,305,962 of 1917.

[48] Christensen, B.P. 132,846, *Brit. J. Phot.* **66** (1919) 639.

[49] Robach, *Brit. J. Phot.* **70** (1923) 363.

[50] Namias, *Brit. J. Phot.* **56** (1909) 68.

[51] Mercer, *Brit. J. Phot.* **42** (1895) 557. Crabtree, U.S.P. 1,389,742.

[52] Lumière and Seyewetz, *Brit. J. Phot.* **73** (1926) 135; **74** (1927) 31. Garnotel, *Brit. J. Phot.* **75** (1928) 153.

[53] This formula and the directions which follow are from "Tinting and Toning of Eastman Positive Motion Picture Film," Eastman Kodak Co., Rochester, N. Y. Fourth edition, 1927.

For use, take 1 part of stock solution and 4 parts water.

Time of Mordanting. Immerse the film (slide) at 65° to 70° F. (18° to 21° C.) until a very slight chocolate-colored tone is obtained and remove at once. If mordanting is prolonged, much beyond this point, inferior tones will be produced. With a new bath, this will require from 1½ to 2 minutes but the time will need to be increased as the bath ages. The solution may be revived at intervals by adding a little of the concentrated stock solution.

Time of Washing after Mordanting. Wash until the highlights are free from yellow stain which usually takes about 10 to 15 minutes. Do not prolong the washing for more than 20 minutes or some of the mordant will be washed out.

The Dye Bath

Dye	0.2 gm.	3¼ oz.	3 gr.
*Acetic acid, 10%	5.0 cc.	76.8 oz.	1¼ dr.
Water to make	1.0 liter	120 gal.	32 oz.

* To convert glacial acetic acid into 10% acetic, take 1 part glacial acetic acid and add it slowly to 9 parts of water.

Thoroughly dissolve the dye in hot water, filter, add the acid and dilute to volume with cold water.

The following dyes are suitable for toning:[54]

Safranine A	Red
Chrysoidine 3R	Orange
Auramine	Yellow
Victoria Green	Green
Methylene Blue BB	Blue
*Methyl Violet	Violet

* For methyl violet use one-quarter the quantity of dye given in the formula.

Time of Dye Toning. Immerse the mordanted and washed film (slide) in the dye bath for 2 to 15 minutes according to the color desired. The quantity of dye which mordants to the image increases with time. In case an image is over-dyed, some of the dye may be removed by immersing in a 0.2% solution of ammonia; then rinse after drying.

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[54] The dyes listed are obtainable from Eastman Kodak Company, Rochester, N. Y., in quantities under one pound. Larger quantities should be purchased directly from the manufacturer, National Aniline Co., 40 Rector St., New York, N. Y.

If, after dyeing 10 minutes, the image does not mordant sufficient dye, remove the film (slide), wash thoroughly, immerse again in the mordanting bath, wash, and re-dye.

Intermediate Dye Tones. Intermediate colors may be obtained either by mixing the dye solutions or by immersing the film (slide) in successive baths. For example, if a reddish-orange tone is desired, first tone for a short time in the Safranine bath and then in the Chrysoidine bath, or the two baths may be mixed in suitable proportions and the tone secured with a single treatment.

Dye Toning in Single Solutions.—It is possible to combine the mordanting and dye baths to form a single solution toning bath. The difficulty in most cases is the precipitation of the dye. A satisfactory method has been described by Crabtree and Ives.[55]

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[55] *Trans. Soc. Mot. Pict. Eng.* **12** (1928) 967. Dye toning may be combined with various processes of chemical toning. Crabtree and Marsh, *J. Soc. Mot. Pict. Eng.* **14** (1931) 57.

CHAPTER XXV

PRINTING PROCESSES: CARBON, GUM-BICHROMATE, BROMOIL, ETC.

The Carbon Process.—Ever since its introduction as a practical process, carbon has been recognized as one of the finest of printing mediums. In common with other processes, which depend upon the action of light upon chromic salts, the carbon process affords a wide variety of colors and surfaces. But even more important is the fidelity with which carbon reproduces the delicate tones of a negative. In this respect the carbon process is unsurpassed.

There are two variations in carbon printing known as single and double transfer. In the first case the image is reversed from right to left, while in the latter instance the image is non-reversed. Carbon tissue consists of paper coated with gelatin and pigment. Before use, it has to be sensitized in a solution of potassium bichromate and is then dried in the dark. With a spirit sensitizer, drying is very rapid and sensitizing is in operation which requires very little time. When dry, the tissue is exposed to daylight under the negative, a photometer being used to regulate the exposure, as the image is not visible. When exposure is complete the tissue is removed from the frame and allowed to soak until limp in cold water. In the meantime, a sheet of single transfer paper, or the temporary support if double transfer is to be made, is allowed to become pliable in the water. As soon as limp, the two are brought together and pressed into contact. After remaining under pressure a short while, the two are immersed in warm water and the tissue stripped off, leaving the gelatin and pigment adhering to the transfer paper, or to the temporary support in case of double transfer. Gentle washing in the warm water follows and the unacted upon bichromated gelatin with its pigment soon washes away, leaving the image in pure insoluble pigment. As soon as development is complete, the print is removed, placed in a bath of alum to remove the bichromate stain and harden the gelatin and is finally dried. Double transfer is a little more complicated. After development on the temporary support, the image is hardened and allowed to dry. It is then again placed in water and brought in contact with a sheet of double transfer paper.

The two are allowed to dry in contact and the paper may then be stripped from the temporary support carrying with it the image. Carbon is a comparatively simple and straightforward process and instructions unfortunately make it appear more involved than it really is.

The chemical reactions involved in the tanning or insolubilizing of a bichromated colloid upon exposure to light are still not definitely known. The neutral chromates, with the exception of ammonium chromate which decomposes in solution into ammonium bichromate, do not sensitize gelatin and the bichromates are not light sensitive except in the presence of organic matter. The investigations of Eder, Lumière, Seyewetz and others suggest that the bichromate or chromic acid is reduced to chromium sesqui-oxide Cr_2O_3, which then reacts with excess bichromate or to form a chromium chromate, which may be Cr_2CrO_6, and is the actual tanning or insolubilizing compound.

$$2H_6CrO_6 + \text{Light} \rightarrow Cr_2O_3 + 6H_2O + 3O,$$
$$Cr_2O_3 + CrO_3 \rightarrow Cr_2CrO_6 \rightarrow (3CrO_2).$$[1]

Sensitizing Carbon Tissue.—Carbon tissue sensitized with potassium or ammonium bichromate does not keep well, becoming insoluble in a few days. The use of a neutral chromate such as potassium chromate results in a more stable tissue but of much lower sensitiveness. The sensitiveness may be increased, however, by suspending the tissue, before exposure, over a tray of glacial acetic acid in a closed chamber.[2]

Both the ammonium and potassium salts are used; ammonium bichromate is the more sensitive but the potassium salt is generally used on account of its cheapness. The ammonium salt is more soluble in water, which is an advantage in a spirit sensitizer as a larger amount of alcohol or acetone may be added without causing precipitation. The sensitiveness of tissue sensitized with potassium bichromate is increased by the addition of ammonia or ammonium carbonate.[3] Too much of either reduces rather than increases the sensitiveness of the tissue; approximately 0.2% of ammonia (20 cc. to 1000 cc.) or one half the quantity of ammonium carbonate may be used. The tissue also keeps better, as the occurrence of free chromic acid is prevented.

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[1] Sheppard, *Photography as a Scientific Implement,* p. 171.
[2] Namias, *Brit. J. Phot.* **67** (June 1920) 306.
[3] Lumière and Seyewetz, *Eder's Jahrbuch* (1906) 184.

WALL—The Chromium Salts. Amer. Phot. **16** (1922) 613.
MIDDLETON—Some Experiments and Notes on Pictures in Pigments. Brit. J. Phot. **70** (1923) 735.

The sensitiveness and also the contrast vary with the concentration of bichromate in the sensitizing bath.

Concentrated solutions (4 to 6%) result in greater sensitivity and low contrast; a dilute solution (1 to 2%) produces higher contrast, although the time of exposure is longer. Contrast is affected to a certain extent by the color of the pigment; those which absorb blue and violet strongly tend to produce greater contrast.

If the tissue is to be used as soon as dry, a solution of potassium or ammonium bichromate may be used; if, however, it is to be kept for three or four days, a trace of ammonia (about .02%) should be added.

The tissue may be sensitized by immersing it in the sensitizing solution, or the solution may be applied with a brush. Quick drying sensitizing solutions containing alcohol or acetone are usually applied with a brush. Tissue sensitized with a plain solution of bichromate requires several hours for drying, while with a quick drying sensitizer drying is usually complete within one-half to three quarters of an hour. For the occasional worker the use of rapid drying sensitizers is recommended.

Methods of Increasing Sensitiveness of Carbon Tissue.—The addition of a mild reducing substance to dichromated gelatin results in increased sensitiveness. Among the substances employed have been potassium ferrocyanide,[4] copper sulfate, copper chloride and cobalt chloride.[5] F. J. Tritton recommended that the tissue, after sensitizing in a 2% solution of dichromate and exposing for ⅓ the usual time, be placed in a 2% solution of cerous chloride for mounting instead of water. The time of immersion is stated to be practically without effect in the density or gradation of the image.[6]

Exposing the Tissue.—With single transfer the print is reversed from left to right. With many subjects this is not objectionable. It may be prevented in the case of film negatives by reversing the position of the negative and printing from the back. Glass negatives may be printed from the back also if a single source of light such as an electric arc is used at a distance of several feet and the printing frame is not moved during the exposure.

[4] Weingarten, U.S.P. 1,564,161 of 1925.

[5] Valenta, *Phot. Korr.* (1914) 327. Eder, *Phot. Korr.* (1914) 326.

[6] *Brit. J. Phot.* **76** (1929) 361. Luxor Film G.M.B.H. patented the fuming of dichromated gelatin layers with an organic acid, such as acetic, after exposure and before development to reduce the exposure. B.P. 289,858 of 1927.

Warburg—Dyes as Sensitizers of Carbon Tissue. Phot. J. **57** (1917) 169.

A mask must be used in printing to prevent the pigment image from leaving the support during development. The mask should be at least ½ inch wide.

Either daylight or strong sources of artificial light such as the white flame arc, mercury vapor tubes, or Photoflood lamps may be used for the exposure. When daylight is used, diffused light is preferable to direct sunlight which may cause the tissue to become insoluble. The tissue must be kept dry while exposing and in damp weather a sheet of waxed paper, or cellophane, should be placed back of the tissue. A substantial printing frame with strong springs is required to ensure good contact between the stiff tissue and the negative.

When printing by daylight the time of exposure must be determined by means of an actinometer which consists of a scale of numbered densities. A strip of printing-out paper is placed beneath the density scale and exposed to light beside the printing frame. The amount of exposure is determined by examining the paper strip and noting the highest number visible in the print-out image. The number which represents the proper exposure for a particular negative must first be determined by trial. With experience it may be estimated with a fair degree of accuracy.

With artificial light it is usually sufficient to expose by time. Special precautions should be taken to avoid heating the tissue which results in a general veiling of the image from the insolubilizing of the pigmented gelatin. When using an arc or Photoflood lamp, a fan may be used to cool the printing frames.

The sensitiveness of the tissue depends upon (1) the concentration of the sensitizing solution, (2) the age of the tissue, (3) the temperature, (4) the color of the tissue. Other things being equal the time of exposure is less for violet and blue than for black, brown or red tissues.

Transfer.—Transfer is necessary because the insoluble pigment which has been formed by the action of light is upon the surface of the

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BEKK—Sensitometry of the Pigment Process. Klimschs Jahrbuch **28** (1935) 119.

BOUECK—Sensitometry of Bichromate Gelatin. Proc. Ninth Int. Congress of Phot. Paris. 1935. Sci. et Ind. Phot. (II) **6** (1935) 327.

HARDY AND PERRIN—Sensitometry of the Bichromated Gelatin Process. J. Franklin Inst. **205** (1928) 197–219.

KEILICH—Researches on the Characteristic Curves of Pigment Processes. Z. wiss. Phot. **37** (1938) 195.

tissue while the insoluble pigment which must be washed away in order to reveal the image lies beneath the image. It is, therefore, necessary to transfer the pigment so that the soluble pigment will be on top where it can be washed away without affecting the pigment forming the image.

In single transfer, the exposed tissue is transferred directly to the final support; in double transfer the image is first transferred to a temporary support on which it is developed by washing away the soluble gelatin in warm water. From this temporary support it is transferred a second time to the final support.

We will deal with single transfer first.

The final support may be the gelatin coated transfer paper obtainable from dealers, opal, glass, porcelain or metal. These latter must first be coated with a 3% solution of bichromated gelatin which after drying should be exposed to light for several hours to render the gelatin layer insoluble.

A sheet of single transfer paper is placed in cold water at about 60° F. (16° C.) for several minutes until it is limp. The exposed tissue is then placed in the same water. The tissue will at first curl inward and then outward until it becomes practically flat. At this point it should be removed from the water and placed face down upon the transfer paper, which should have been previously placed upon a flat surface with the side coated with gelatin upwards. When the two are in contact, a squeegee is passed over the same from center to the margin with moderate pressure in order to eliminate air and moisture. After being squeegeed into contact the tissue and its support may be placed under blotters and allowed to remain for 15 to 20 minutes before development.

Development.—Place the tissue and its support in water at about 95° to 100° F. (35° to 38° C.). In a few seconds the pigment will begin to ooze out around the edges. When this begins, separate the corner of the tissue and its support by lifting it with the finger nail and pull off the paper that originally held the pigmented gelatin. This tissue may be discarded. Holding the print by one corner, gently splash warm water over the surface. The soluble pigment will gradually wash away leaving the image. Care should be taken not to touch the print with the hands or any hard substance as the gelatin is very soft and easily injured at this stage. If the print is underexposed, the pigment will wash away very easily while if exposure is excessive the pigment dissolves with difficulty and warmer water must be used. Highlights may be lightened or detail in dark shadows may be brought out at this stage by squirting water from a blow tube against the print, or hot water may be poured on the desired portion.

If the image is too dark, overexposure is indicated. A light print with clear highlights from which the pigment has completely disappeared indicates underexposure, or developing in water above the proper temperature. Prints which are slightly overexposed may sometimes be improved by raising the temperature of the water during development or by adding a few drops of ammonia or a 2% solution of ammonium persulfate.

When development is complete, place the prints in clean cold water for a minute and then transfer to a 5% solution of alum to remove the bichromate stain and harden the gelatin. Porcelain steel enamelled or hard rubber trays may be used for the alum solution but tin or zinc vessels, such as may be used for development, are to be avoided. The time required in this bath varies, but sufficient time should be given to make sure that all of the bichromate stain has been removed as any trace which is left will be more noticeable when dry than while wet.

After clearing and hardening in the alum bath, the print is removed and well rinsed in water and then hung up to dry. Carbon prints should not be forced in drying by heat as there is a danger of the gelatin cracking. An electric fan, however, may be used to hasten the process.

Double Transfer.—Before development, instead of being attached to the transfer paper, the exposed carbon tissue is fixed to a temporary support. This temporary support may be opal glass or the specially coated paper supplied by the Autotype Company.

Before use, the support must be waxed so that the gelatin image may be stripped from the temporary support without danger when transferring to the final support. The waxing solution consists of one part of beeswax and three parts of resin dissolved in turpentine and may be purchased especially prepared. Several drops of this waxing solution are poured on the temporary support and gently rubbed over the surface using a pad of flannelette. The waxing is a simple operation but care must be taken that the support is evenly and thoroughly waxed. If a part of the support has not been covered at all the gelatin may adhere and the print will then be spoiled. An hour or so must be allowed after waxing before the supports are used in order to allow the turpentine to evaporate. It is an excellent plan to wax the supports several hours, or on the day before they are to be used.

There is less latitude in development with double than with single transfer and the exposure should be as nearly correct as possible in order that very hot water may not be necessary for development. There is a tendency for the image to blister while on the temporary support which is due to a softening of the wax and the use of hot water, of course, will cause the wax to soften more than cold.

The temporary support is placed in water along with the exposed tissue and allowed to remain until it becomes comparatively flat. The exposed tissue is then squeegeed to the waxed side of the temporary support and allowed to remain under pressure for several minutes after which it is developed in exactly the same way as single transfer. After development, the temporary support with its adhering image is placed in the alum bath to discharge the bichromate stain and harden the gelatin, after which it is rinsed and allowed to dry. Care should be taken not to injure the delicate surface during any of these operations. Dry the image in a cool place—not in the sun nor by any kind of heat.

When dry, the operation of transferring the image to the final support may be proceeded with. For this purpose double transfer paper is supplied in a wide variety of tones and surfaces. The sheet of double transfer paper should be larger than the temporary support, say 7 × 9, for 5 × 7 print. It is placed in cold water and allowed to soak for an hour in order to swell the gelatin coating so that the image will adhere. After soaking for an hour remove and place for a minute or so in water at about 90° F. until the surface feels slimy to the touch after which it is again returned to the cold water where it may remain until required. The dry print on the temporary support is now placed in cold water until flat and limp and is then taken out and placed face up upon a smooth flat surface as a sheet of plate glass. The sheet of softened double transfer paper is then placed on top of it and held in place by one hand while the two are squeegeed into perfect contact with a flat squeegee. The pressure must be sufficient to force out the water but not so great as to affect the gelatin. A few trials will serve to show the proper amount of pressure to apply. The temporary support and double transfer paper are then hung up on a line to dry. When thoroughly dry, insert the point of a knife blade under one corner and pull the two apart, when it will be found that the image leaves the temporary support and adheres to the double transfer paper. If the plate has not been properly waxed, the image may adhere to the temporary support in places and the print ruined. This may also happen if the gelatin coating of the double transfer paper has not been sufficiently softened before use.

The Gum Pigment Process (Gum-Bichromate).—The gum bichromate process is one of several which depend upon the action of light on a bichromated colloid. Unlike carbon and carbro, there is no transfer, and multiple printing is necessary in order to secure a full scale of gradation. As a printing medium the gum-bichromate process is one of the most flexible and is especially noteworthy for its ability to produce deep, rich shadows without any trace of muddiness. It is, however, a rather tedious process and in recent years has been used less and less.

Preparing the Paper.—Rough water color or charcoal papers, depending upon the size of the print and the amount of detail desired, are suitable.

The paper is coated with a sizing solution, the following being a suitable formula.

Bermuda arrowroot	18.7 gm.	90 gr.
Water	1000 cc.	10 oz.

Using a little of the water, make a thin cream of the arrowroot. Then heat the remainder of the water to the boiling point and add to the arrowroot mixture. As the solution does not keep, it must be made up fresh for each batch of paper sized. The sizing solution is best applied with a Blanchard brush.

After sizing, the paper is coated with a mixture containing pigment of the color desired, gum arabic, and potassium bichromate. The proportions vary with different workers and according to the paper, the negative, and the effect desired. The formulas which follow are due to Paul L. Anderson.

Gum Solution

Gum-arabic	336.6 gm.	2200 gr.
Arrowroot	44.6 gm.	270 gr.
Mercuric chloride	2.5 gm.	15 gr.
Water	1000 cc.	12 oz.

Dissolve the mercuric chloride in a small amount of water and then add the arrowroot, stirring the same until a thin cream is obtained. Then add the remaining water and the gum-arabic. The latter will dissolve more rapidly if suspended in the solution by means of a cheesecloth bag. From 16 to 24 hours will be required for the latter to dissolve completely.

Sensitizing Solution.—The stock solution of sensitizer consists of a solution of potassium bichromate:

Potassium bichromate	96 gm.	720 gr.
Water (hot)	1000 cc.	15 oz.

Both of these solutions keep well.

The actual mixture used for coating varies with the paper and the negative and also with the effect desired. Practically every worker develops a different formula after practice and while there may be little difference, yet it is better adapted to his own personal methods of working.

However, the following formulas are given for the benefit of the beginner:

Shadow Coating

Gum solution	15 c.c.	½ oz.
Sensitizer	15 c.c.	½ oz.
Ivory black from tube	4 in.	4 in.

If the negative has a short scale of gradation it may be possible to use the above for all the printings; if, however, this is not the case and the negative has a long scale of gradation and prints well with bromide or platinum, then it will be necessary to vary the coating mixture so as to secure a longer scale. It is generally necessary to make three printings: one for the shadows, another for the halftones and finally one for the highlights. The following are advised for the halftone and highlight coating mixtures.

Halftone Coating Mixture

Gum solution	15 c.c.	½ oz.
Sensitizer	15 c.c.	½ oz.
Ivory black from tube	2 in.	2 in.

Highlight Coating Mixture

Gum solution	15 gm.	½ oz.
Sensitizer	17.75 cc.	5 dr.
Ivory black from tube	1 in.	1 in.

Increasing the amount of pigment in the coating mixture results in a longer range of tones, but the whites tend to be degraded.

Increasing the amount of gum arabic results in greater contrast, while an excess produces a thick film which may chip off in development Increasing the proportion of potassium bichromate results in decreased contrast; an excess produces flat, lifeless prints.

Coating.—The coating mixture having been prepared, the sensitizing of the paper may proceed. Rough papers are the easiest to coat and the beginner is therefore advised to start with rough paper, as Whatman's. The sheet should be larger than the negative as it is next to impossible to secure a perfectly even coating to the very edge of the paper. A sheet 11 × 14 will be suitable for either 8 × 10 or 10 × 12, while an 8 × 10 sheet is sufficiently large for a 5 × 7. Attach the paper to the drawing board with push pins and pour the coating mixture in the center. The paper will be more easily coated if it is immersed in water and blotted before being placed on the board. For the first 11 × 14 sheet of paper, about one half ounce of the coating mixture will be required, while succeeding sheets will require somewhat less, owing to the brushes becoming charged with the gum. The rubberset bristle brush is used to spread the coating over the paper so that every part is covered with the coating mixture. When this has been done, the blender comes into play. There are two brushes which may be used for blending (one made of fitch and the other of badger) and the details of the operation depend somewhat upon which is being used. With the former the brush is held nearly vertical and drawn slowly and regularly across the paper—always in the same direction. When the sheet has been covered in one direction, it is again gone over in the opposite direction, to secure a perfectly even coating. With the latter, the action may be "whippy," the vigorous handling of the brush lessening as the operation proceeds. The exact manner of handling the brush and the time to stop blending will come with a little experience. In general, it may be said that when the point is reached where the tendency of the gum solution is to run into small puddles, the operation should be stopped whether the surface appears completely even or not. Any irregularity will disappear in drying or development or will be covered by subsequent printings. As soon as the operations

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Anderson—The Gum Pigment Process. Amer. Phot. **7** (1913) 504, 584, 648, *700*, *707*; **8** (1914) 8, 12, *76*.

Batty—A Simplified Method of Printing in the Gum-Bichromate Process. Phot. J. **63** (1923) 398.

Grandmaitre—Multi-Layer Gum Process. Bull. Soc. franç. Phot. **10** (1923) 16.

Leighton—A Method of Working the Gum-Bichromate Process. American Annual of Photography (1924) 40

Libby—Multiple Gum American Annual of Photography (1922) 124.

Starnes—The Gum-Bichromate Process and a New Colloid. Phot. J. **58** (1918) *287*; Brit. J. Phot. **66** (1919) 50.

are complete the utensils should be washed free from the gum solution, as it is very difficult to remove when dry.

The coated paper should be placed in a dark, dry, and dust-free place where there is a good circulation of air to dry. From one to two hours will be required for drying at ordinary room temperature. If it is not to be used at once, the paper should be stored in an air-tight container such as used for carbon tissue. The coating is at its best when fresh.

Exposure and Development.—When exposing by daylight an actinometer of the type used in carbon printing must be employed to determine when the coating has been properly exposed. Artificial lights such as the white flame arc and mercury vapor tubes may be used, and in this case it is sufficient to expose by time. There is a good deal of latitude in exposure, but correct exposure enables water at ordinary temperature to be used for development and produces the best results. Overexposure may be compensated for to a certain extent by raising the temperature or the addition of a few drops of ammonia to the water. An underexposed print is useless as the image washes away in development.

To develop, the exposed print is placed face up in a large tray of clear water at a temperature of about 65° F. When limp it is turned face down, care being taken that no air bells are imprisoned beneath it. From time to time it may be examined and transferred to a tray of clear water. From ½ to 1 hour will be required for the complete development of a properly exposed print. If the image appears fully developed in 10 or 15 minutes the print is underexposed and may as well be thrown away. If the image does not appear in 30 to 40 minutes, the print has been overexposed.

When the solution which drains from the print when removed from the water is practically clear, development may be considered complete.

To lighten any local portions the print may be held under water and a stream of water from the tap allowed to fall upon the desired portion, or an atomizer used. Greater emphasis may be secured by using hot water or by holding the print so that the stream of water falls directly upon the surface. Local values may also be lightened by the use of a very soft brush. There is a tendency for brush work to show graininess and for that reason it should be avoided whenever possible.

If it is desired to darken any part, the coating mixture may be prepared and applied by means of a brush to the desired portions and the whole exposed to light when dry. It is then washed in water for about half an hour and dried in the regular way. It is necessary to include the sensitizer in order to secure the same tone as the original deposit.

Multiple Printing.—Gum-bichromate is a short scale process and to render a full scale of tones, or to obtain the rich luminous shadows which are characteristic of the process, multiple printing must be resorted to. Usually the result desired may be obtained in 3 printings, one for the highlights, one for the middle tones, and one for the shadows; but at times 4 or 5 printings may be necessary. The proportions of gum and pigment and sensitizer in the coating mixture vary for the different printings as shown in the formulas on p. 670.

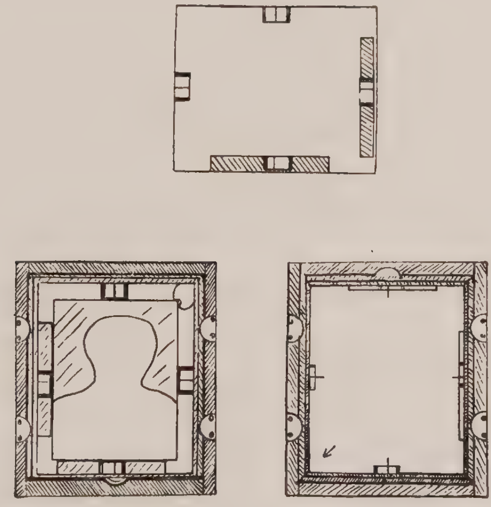

Fig. 342. Method of Registering Paper and Negative for Multiple Printing.

It is necessary in multiple printing to provide means for ensuring the accurate superimposition of the images produced by the different printings. Many methods have been devised for this purpose.[7]

Perhaps as satisfactory a method as any is to use a printing frame several sizes larger than the negative. The negative is attached to the glass, and near the middle along each side is placed a strip of white paper. Prior to the first printing the coated paper is placed in position over the negative and registration marks placed on each of the four sides as shown in Fig. 342. In this way any shrinkage which may take place between printings is distributed from the center.

[7] Owen, *Amer. Phot.* (1923) 416. Zerbe, *Amer. Annual Phot.* 37 (1923) 123.

Gum Bromide and Gum Platinum.—To avoid the difficulties of multiple printing many workers have combined gum printing with bromide or platinum, using a print made by one of these processes as a foundation to supply the necessary depth to the shadows and middle tones and a superimposed gum pigment image to secure the characteristic appearance of a gum pigment print.

Before exposure the bromide or platinum paper, as the case may be, is placed upon the negative and its position registered by any of the means already considered. It is then exposed and developed in the usual way, to produce an image of the required intensity.

When dry the print is ready for the gum pigment coating. The proportions of gum and pigment in the coating mixture depend upon the depth of the foundation print and the effect desired. The gum pigment coating is dried, exposed, and developed in precisely the same way as a gum-pigment print.[8]

Miscellaneous Pigment Processes.—*Glue Printing:* This is a modification of the gum pigment process developed by Heinrich Kuehn.[9]

Paper is coated with ordinary glue and a suitable pigment. After having been sensitized in a solution of potassium bichromate the paper base is rendered transparent with parafin oil or kerosene and the exposure made through the paper. The image is developed as in the gum pigment process.

Fresson. This non-transfer process of pigment printing is of Belgian origin and has attracted but a small following. A special gum pigment paper is sensitized with a solution of potassium bichromate and exposed by daylight or strong artificial light. After exposure, the print is placed in a tray of cold water and the temperature gradually raised to approximately 85° F. After three or four minutes immersion the pigmented layer becomes "tacky" in places and the print is removed and placed on a sheet of heavy glass. Water containing finely ground sawdust is then poured over it. The gentle abrasive action of the sawdust removes the softened pigment and gradually brings out the image. The image has a pronounced grain or texture which, however, is not displeasing with certain subjects.[10]

Resinopigmentype. In this pigment process, developed by Prof. Rudolph Namias, of Milan, a gelatin coated paper is sensitized in potassium or ammonium bichromate, dried and exposed under a positive transparency. It is then placed in cold water for several hours to eliminate the excess bichromate and transferred to water at 50° C. (122° F.) to produce a brief image in differentially hardened gelatin. A resinous pigment, impervious to water (as gum dammar, shellac, bitumen or dragons blood with a suitable pigment) is then applied with a brush. The pigment adheres to the swollen portions of the image (after the surface moisture is removed) but not to the hardened portions, thus forming a pigment image.[11]

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[8] Davis, "Gum Bromide Printing," *Amer. Phot.* **15** (1921) 53. Zerbe, "Gum Platinum," *Amer. Phot.* (April 1910.)

[9] Kuehn, *Technik der Lichtbildnerei*, Innsbruck (1921) 39. Richter, "The Glue Print," *Amer. Phot.* 17 (1923) 38.

[10] Mauret, *Amer. Annual of Phot.* 43 (1929) 179.

Sury's Process.[12] J. Sury, of Belgium, patented in 1914 a powder process in which paper was coated with gelatin, gum arabic, or albumen to which was added a fine colorless powder to produce an inert and matt surface. The paper was sensitized in a bichromate, dried and exposed under the negative to daylight or strong artificial light. After exposure the paper was washed in water to remove the soluble portions of the colloid and dried. Finally, pastel colors were applied, the powder added to the colloid coating providing a "tooth" and the image worked up. The process attracted only a small following and the paper is no longer available commercially.

Powder Processes. Practically none of the processes described in the older works on photography have survived nor is there much interest in the subject today. It may be useful, however, to call attention to the fact that a developed silver image, such as a bromide print, may be converted into one which will accept an inert pigment by bleaching in ferric chloride and tartaric acid,[13] ammonium persulfate, and peroxide.[14] Wall recommended the following process [15]

The bromide print, which should have been fixed in plain hypo and not in an acid fixing and hardening bath, is transferred directly from the last wash water to the following solution:

Cupric sulfate	5	gm.	28	gr.
Nitric acid	6	cc.	45	min.
Potassium bromide	0.5	gm.	4	gr.
Hydrogen peroxide	100	cc.	1⅗	fl. oz.
Water to make	1000	cc.	16	oz.

which should be used at a temperature of 70° F. (21° C.). From 5–20 minutes in this solution are required depending on the emulsion.

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[11] Namias, B.P. 205,092 of 1922; *Brit. J. Phot.* **72** (1925) 220.

[12] B.P. 21,958; *Brit. J. Phot.* **61** (1914) 748.

[13] Capstaff, U.S.P. 1,315,464 of 1919.

[14] Liesegang, *Phot. Archiv.* **39** (1897) 161. Andresen, D.R.P. 103,516 of 1898.

[15] *Amer. Phot.* **18** (1924) 428.

For the powdering of the image any inert pigment, black or colored, may be used, but it should be as finely ground as possible, or the results may show an undesirable amount of grain. The powder may be applied either with a very soft brush or by means of a little sieve having a bottom of the finest muslin. Some of the powder is placed in the sieve which is held over the image and tapped with the finger. This method is perhaps preferable when using a pigment containing rather coarse particles.

Chemistry of Processes Based upon the Insolubilization of Bichromated Colloids by Finely Divided Silver.—Carbro and bromoil are the most important of a number of printing processes, based upon the discovery by Howard Farmer, in 1889, that in the presence of gelatin, the bichromates are reduced by finely divided silver so that when a bromide print is immersed in a solution of bichromate, the gelatin in contact with the silver image is rendered insoluble without exposure to light.[16]

In the carbro process (carbon from bromide prints) the carbon tissue is sensitized by immersion in a solution of potassium ferricyanide, potassium bichromate and potassium bromide. The tissue is then placed in contact with the wet bromide print. While the two are in contact certain chemical reactions take place which produce an image in the carbon tissue similar to that formed upon exposure to light under a negative. The carbon tissue after having been transferred to a suitable support is developed as in the carbon process. The carbro process thus provides a means of making carbon prints from a bromide print, utilizing the finely divided silver of the bromide print rather than light as the means of differentially hardening the gelatin.

[16] B.P. 17,773 of 1889.

BULLOCK—Theory of the Carbro Process. Phot. J. **67** (1927) 213.

MURRAY AND SPENCER—The Hardening of Gelatine by Means of Copper-Dichromate Solutions. Phot. J. **73** (1933) 497.

LIGHTON—Theory and Practice of the Carbro Process. Phot. J. **67** (1927) 362, 409.

SCHIEL—Bromoil Printing. Phot. Rund. **63** (1926) 55–58, 97–99, 182–186.

SCHIEL—Chromic Acid Bleach and its Reaction Product. Phot. Korr. **63** (1927) 117–120.

SCHROMMER—Gelatin Hardening in Chromate Processes. Phot. Rund. **63** (1926) 120, 138.

TRITTON—Theory of the Carbro Process. Phot. J. **66** (1926) 126.

VENN—Further Researches in the Bromoil Process. Brit. J. Phot. **73** (1926) 384, 401.

In the bromoil process, a bromide print is bleached in a solution containing a bichromate, or chromic acid, potassium bromide and either potassium ferricyanide or a cupric salt, usually the chloride or the sulfate, which results in the tanning of the gelatin in contact with the grains of silver, thus producing an image in differentially hardened gelatin. The bromide print is then soaked in water which is repelled by the unhardened gelatin. An oil pigment is then applied with a brush. The pigment adheres to shadow portions of the image but is repelled by the highlights which are more or less saturated with water. Thus there is built up a pigment image on one of differentially hardened gelatin.

From a chemical standpoint the two processes are essentially the same; the mechanism of the two processes, however, is somewhat different, as in bromoil the insolubilization of the gelatin takes place in the film containing the image, while in the carbro process the insolubilization has to be produced in another layer of gelatin by diffusion.

The probable reaction here is first the bleaching of the silver image, resulting in the formation of silver bromide and potassium ferrocyanide. This is reoxidized by the bichromate back to ferricyanide, the reduction of the bichromate resulting in the insolubilization of the gelatin. With copper salts the reaction is essentially the same, the cupric salt and bromide reacting with the silver image to form cuprous bromide, which is reoxidized by the bichromate into a cupric salt, the reduction of the bichromate resulting in the insolutbilization of the gelatin. Hypothetical reactions can, and have been, written to represent these reactions but the objection to all such equations is that while they show what can take place, there is little evidence to show that it does take place. Consequently, it does not seem worth while, at the present time, to attempt to represent the reaction in the form of a chemical equation.[17]

The Carbro Process.—Any standard make of smooth or semi-matte bromide paper is suitable, for the bromide print, although one without a super coating (non-abrasion) is preferable. The super coating occasionally results in granularity and a loss in the highlights. Some improvement may be effected by making the print darker.

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[17] Namias, *Phot. J.* **42** (1912) 57; *Brit. J. Phot.* **59** (1912) 217. Eder, *Handbuch,* **4** (1917) 279. Venn, *Brit. J. Phot.* **71** (1924), 427; **72** (1925) 119. Lighton, *Phot. J.* **66** (1926) 545; **67** (1927) 362. Tritton, *Phot. J.* **66** (1926) 126. Schömmer, *Phot. Rund* **63** (1926) 120, 138. Schiel, *Phot. Rund.* **63** (1926) 55, 97. Mayer, Bromoil Printing and Transfer, American Photographic Publishing Co., Boston. Murray and Spencer, *Phot. J.* **73** (1933) 497. Bullock, *Brit. J. Phot.* **70** (1923) 491.

If developing-out papers of silver chloride are used, the print should be made darker than would be necessary for a bromide print, and before use, it should be bleached in the usual ferricyanide-bromide solution as used for sepia toning (page 651) and redeveloped in an ordinary developer.

The print, whether on a bromide or a chloride paper, should receive full exposure and development. A slight burying of the gradations in the shadows is not objectionable as these gradations will be retained in the pigment image.

Where the water supply contains lime, it is well to place the print, after fixing and washing, in a solution of hydrochloric acid and water (3 parts concentrated hydrochloric acid to 100 parts of water) for 5 minutes, then wash for 10 minutes. If this is not done there is a danger that the lime formed within the bromide print will prevent complete bleaching of the highlights with the result that they wash away in the development of the carbro.

Should any spotting be required, or it is desired to darken certain portions in such a way that the result will be reproduced in the carbro print, one may use water color containing India ink. All such alterations are reproduced in the carbro print with as complete transference as any part of the image.

Sensitizing the Carbro Tissue.—For this purpose the following stock solutions are required:

Concentrated Solution No. 1:		
Potassium bichromate	10 gm.	1 oz.
Potassium ferricyanide	10 gm.	1 oz.
Potassium bromide	10 gm.	1 oz.
Water to make	200 cc.	20 oz.
Concentrated Solution No. 2:		
Glacial acetic acid	10 cc.	1 oz.
Hydrochloric acid (pure)	10 cc.	1 oz.
Formaldehyde 40%	220 cc.	22 oz.

The addition of 1¼ oz. or 12 cc. of water to the above will prevent precipitation in cold weather.

BRAHAM—The Carbro Process. Phot. J. **62** (1922) 16; Brit. J. Phot. **69** (1922) 4.

FARMER—The Carbro Process. Amat. Phot. (1919) p. 285; Brit. J. Phot. **66** (1919) 583; Amer. Phot. **14** (1920) 92.

GARON—Revised Formulae for Carbro. Brit. J. Phot. **68** (1921) 327.

LIGHTON—Sharpness of Reproduction in the Carbro Process. Phot. J. **66** (1926) 545.

For use take:

First Bath:		
Concentrated No. 1 stock solution	100 cc.	6 oz.
Water to make	300 cc.	18 oz.
Second Bath:		
Concentrated No. 2 stock solution	10 cc.	1 oz.
Water to make	320 cc.	32 oz.

The above English and metric weights are not equivalent but are proportionate.

The first bath may be used for a number of prints, but the second bath is affected by the number one bath carried over into it with the pigmented tissue so that it must be renewed frequently.

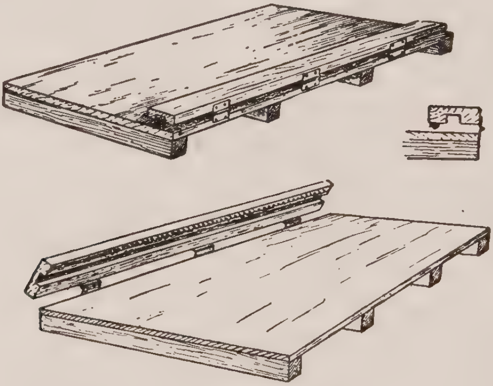
The first and second baths should be as near the same temperature as possible and not colder than 60 F. nor warmer than 70° F. (15° to 20° C.). A low temperature results in light prints lacking in contrast and a high temperature in dark prints with clogged shadows.

The working baths having been made up, the sheet of carbon tissue is immersed in No. 1 bath by sliding it under the surface of the solution. Remove any airbells on the face of the tissue and then turn it face downwards. After two minutes the pigmented tissue should be again turned face upwards and allowed to remain for another minute. Then lift it up by the corner and let it drain for 15 seconds. Finally grasp it by two corners and slide it face up into solution No. 2.

The time of immersion controls the depth and contrast of the carbro print and the correct time in the second bath depends upon the degree of contrast required, the brand of paper employed for the print, the degree of contrast of the print, the hardness of the water, and, to a minor degree, by the number of carbro prints which have been made from the print. The shorter the time of immersion the greater the contrast of the carbro print; increasing the time in the second bath results in less contrast. Prolonged immersion produces a pale and flat carbro print; a short time results in a dense print lacking detail in the highlights which in extreme cases may wash away entirely.

The normal time is from 20 to 30 seconds. If the water supply is very soft the time of immersion is less and under such circumstances the solution may be diluted with one-half the total quantity of water.

Making the Print.—The number of seconds decided upon having elapsed, the pigmented tissue is lifted from the bath and laid upon the bromide print which should have been previously soaked in water for ½ hour and laid upon a sheet of glass or upon the squeegee board illustrated in Fig. 343. Once the two are in contact their relative positions must on no account be altered as the action begins immediately and a change in position would produce a blurring of the image. As soon as the pigmented sheet is in contact with the bromide print a rubber squeegee is brought into play and the superfluous water forced out by firm, straight strokes.



The upper drawing shows the hinging of the clamping strip at the requisite height above the base. In the lower drawing is indicated the edging of studded rubber.

Fig. 343. Squeege Board for Holding Bromide Print and Pigment when Squeeging by Hand.

The bromide print with its adhering sheet of carbon tissue is then lifted from the glass or squeegee board, placed between greaseproof paper and allowed to remain for 15 minutes for the action of the insolubilizing solution to take place.

The proper amount of pressure in squeegeeing is a matter of importance. If the bromide print and the pigmented tissue adhere tightly and force is required to separate them, the pressure has been too great; on the other hand if they tend to separate of their own weight, greater pressure should be applied. Lack of sufficient pressure leads to light carbro prints.

Transfer.—The sheet of transfer paper, which has been soaking in water for at least 15 minutes, is now placed on a sheet of heavy glass, laid flat on the working table, a glass of water poured over it so as to leave a pool of water on the surface. The pigmented tissue is now stripped from the bromide print, squeegeed into contact with the tissue, and placed between blotters under light pressure for 20 to 30 minutes. Heavy pressure leads to difficulty in developing. The longer the time elapsing before developing, the darker the carbro print, as the action continues.

Developing the Carbro.—The carbro print is developed in the same manner as a carbon print (which see) but with water at a lower temperature (95° to 100° F., 35° to 38° C.) as the soluble gelatin leaves the tissue at a lower temperature and more readily than with a carbon print made in the usual way by exposure beneath a negative.

When development is judged to be complete, the print is removed, rinsed in clear cold water and placed in a 5% solution of alum. This removes the yellow stain left behind by the bichromate and ferricyanide and hardens the image. Care should be taken that the action of the alum is complete as the yellow stain is much more apparent when the print is dry than when wet. In commercial practice it is well to use two baths of alum; immersing the print until apparently clear in the first, then transferring to the second for 3 or 4 minutes.

After removal from the alum bath the print should be rinsed well in cold water and hung up to dry. Heat should not be used to hasten drying.

Treatment of the Bromide Print.—Wash the bleached bromide print in water for 15 to 20 minutes and redevelop in the usual developer. Development must be complete. Fixing is unnecessary; after development wash the print for 10 to 15 minutes in running water and dry. When dry it is again ready for use. Succeeding carbro prints will be darker and have greater contrast than the first. This may be overcome by increasing slightly the time of impression in the No. 2 bath.

Carbon on Bromide.—If desired the pigment image can be developed on the bromide print instead of transferring to a new paper support. The procedure is just the same except that when the fifteen minutes of contact between the bromide and the pigmented tissue have elapsed, instead of stripping off the pigmented paper, both it and the bromide print are placed in warm water and developed as already described. The print then consists of a pigment image over the bleached image of the bromide print.

As the yellow color of the bleached image alters the tone of the finished print and since it darkens slightly on exposure to light it is advisable either to redevelop the bromide image or to remove it com-

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NIBBELINK—A Method of Monochrome Carbro. Phot. Tech. **2** (1940) Sept. p. 16.

pletely. Redevelopment of the silver image darkens the print since in this case the resulting print has the depth of the two images; one of silver and the other of carbon.

Causes of Failure with the Carbro Process.—

White Spots: Bubbles or airbells adhering to the tissue during sensitizing or to air being imprisoned between the bromide print and the sensitized tissue. White spots on the carbro are always accompanied by corresponding dark, or unbleached, spots on the bleached bromide.

Dark Spots: Dark spots on the carbro are due to insufficiently washed prints.

Frilling at the Edge: Lack of a safe edge, i.e., white margin on the bromide print.
Bad movement during squeegeeing.

Blisters: Air trapped between the pigment paper and the transfer paper.

The Carbro is Devoid of Highlight Tones: This is due to an excess of lime or chalk in the water used for washing the bromide print. The remedy is to place the bromide print for 5 minutes in a solution of hydrochloric acid (3 parts acid to 100 parts of water) and wash for 10 to 20 minutes in running water. Insufficient immersion in the No. 2 bath.

Light Prints Lacking in Contrast: Weak squeegeeing. Prolonged immersion in the No. 2 solution.

Dark Prints, With Strong Contrast: Insufficient immersion in the No. 2 bath.

Double Image: Shift in the tissue or transfer paper when squeegeeing.

Bromoil.—The bromoil process, in brief, consists in making a good bromide print in the ordinary way, bleaching this in a solution which produces an image in differentially hardened gelatin, and finally applying pigment with a brush to form an image. Owing to the fact that an ordinary bromide print is used, neither daylight nor an enlarged negative is necessary.

The Choice of the Paper for the Bromide Print.—To be suitable for the bromoil process, the bromide paper should have a hard, durable, and well-sized paper base, with an emulsion rich in silver and thickly coated. No hardening substances should be added to the emulsion in the course of manufacture nor should the paper have a super-coating. The bromoil process is based upon tanning of the gelatin in exact proportion to the original silver deposit. If the emulsion has been hardened in manufacture, the gelatin is already tanned to some extent and has lost much of its swelling power, so that it is difficult to obtain the degree of relief necessary for pigmenting.

A number of manufacturers supply bromide papers especially designed for bromoil, and for the beginner these are to be preferred.

To determine whether a particular brand of paper is suitable for bromoil, an unexposed sheet should be dipped in water at a temperature of 86° F. (30° C.) and the behavior of the gelatin observed. If this swells up considerably and becomes slippery and shiny, the paper has the necessary swelling power and can be used for bromoil.[18]

The Bromide Print.—The best bromide print for the bromoil process is one which has received correct exposure and development for a period slightly less than that required for full depth. The shadows should be a deep gray and not the maximum black which the paper will produce. The highlights, on the other hand, should be a trifle darker than would be considered proper for a bromide print. If the factorial method of development is employed, the factor normally employed should be reduced by approximately one-third. Diaminophenol, which is without tanning action on gelatin, is widely used as a developer but metol-hydroquinone may be used. In either case the solution should be fresh, as the oxidation product present in a used developer may result in partial tanning of the gelatin.

The print should be fixed in plain hypo solution or in one made acid by the addition of sodium bisulfite. An acid fixing and hardening bath is to be avoided as, owing to its hardening action, considerable difficulty is experienced in securing the necessary relief.

After fixing, the prints should be thoroughly washed as the slightest trace of hypo will cause trouble in bleaching.

The prints should have a plain white margin of at least one-half inch.

Bleaching Bromide Prints.—The functions of a bleaching solution are two in number: (1) it removes the visible silver image and (2) produces a tanning of the gelatin film in proportion to the amount of silver present in the image.

The usual bleaching solution contains a bichromate (potassium bichromate) or chromic acid, potassium bromide, or sodium chloride, and a cupric salt, usually either the chloride or the sulfate.

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[18] Mayer, *Bromoil Printing and Transfer,* American Photographic Pub. Co., Boston.

Bleaching and tanning may be carried out simultaneously in a single bath or separately in two baths. Of the many formulas for combined bleaching and tanning solutions, two must suffice.

(1) *A.*	Copper sulfate	200 gm.	¾ oz.
	Water to	1000 cc.	3½ oz.
B.	Potassium bromide	200 gm.	¾ oz.
	Water to	1000 cc.	3½ oz.
C.	Potassium bichromate	10 gm.	150 gr.
	Water to	1000 cc.[19]	3½ oz.

For use take:

A	60 cc.	2 oz.
B	60 cc.	2 oz.
C	20 cc.	⅔ oz.
Water to	450 cc.	15 oz.
Hydrochloric acid (conc.)		15 drops

(2) Copper sulfate (10% solution)	96 cc.
Potassium bromide (10% solution)	73 cc.
Chromic acid (1% solution)	27 cc.
Water to make	1000 cc.[20]

The following formulas for bleaching and tanning in separate operations are due to Venn.[21]

Bleaching Solution (No. 1)	
Cupric sulfate (10% solution)	95 parts
Potassium bromide (10% solution)	5 parts
Tanning Solution (No. 2)	
Potassium bromide (10% solution)	20 parts
Potassium bichromate (1% solution)	10 parts
Water to make	100 parts

The first bath may be used for a number of prints in succession; the second should be renewed more frequently.

The temperature of the bleaching and tanning solutions should be uniform and between 55° and 65° F.

Approximately 5 minutes will be required in the second bath, after which the prints should be washed thoroughly in running water, and then fixed for 2 minutes in a 10% solution of hypo. If the print is not washed thoroughly before being placed in the fixing bath, general tanning will be produced through the interaction of the hypo and the substances remaining in the print from the tanning solution. An acid fixing and hardening bath must not be used for fixing.

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[19] Mayer, *Bromoil and Bromoil Transfer.*

[20] Crowther, *Amateur Photography* (1921) 446.

[21] *Brit. J. Phot.* **71** (1924) 427.

After fixing, the print should be washed in running water for 5 to 10 minutes and dried. Some papers do not need to be dried at this stage but it is usually advisable.

Producing the Relief.—When ready to begin pigmenting, the print is immersed in water and the gelatin allowed to swell. The degree of swelling is controlled principally by the temperature of the water and, to a lesser extent, by the time of immersion. The higher the temperature of the water in which the print is soaked, the greater the swelling and the more pronounced the relief. With insufficient immersion, or the use of cold water, the degree of swelling will be insufficient and such prints will, when pigmented, have a short scale of gradation with poor tones. The use of excessively warm water, on the other hand, will produce a pronounced relief which, when inked up, may produce a result having greater contrast than is desirable.

If the degree of relief is correct, the print will accept the pigment from the brush readily and in doing so will differentiate between the highlights and the shadows. After bleaching and washing, the white margins should be very slippery to the touch. If the print is held up by one corner, the straight edge on the margin should be plainly visible.

To determine whether the print is in the proper condition for pigmenting, Dr. E. Mayer suggests that the tip of the finger be passed over the surface gently. With a print in the proper condition the deep shadow portions will feel like very fine sandpaper, that is, grainy and slippery, jelly-like in the highlights, and particularly so along the clear margins.

Water too warm causes over-swelling and the highlights do not take the ink.

The vital factor in putting the print in shape for pigmenting is the adjustment of the swelling of the gelatin to the viscosity of the pigment. Either the print may be soaked at a fixed temperature and the consistency of the pigment adjusted to suit the degree of swelling, or the degree of swelling is adjusted by variation in temperature of the water bath in which the relief is raised to suit the pigment as supplied.

Different papers vary as regards the temperature necessary for producing the best relief. Some are ready for pigmenting after soaking for several minutes in water at ordinary room temperature. Others require as high as 90° F. (32° C.) or more; the general average being about 75° to 80° F. (24° to 27° C.). The worker must learn by experience the temperature to use for his particular brand of paper and manner of working, always remembering that it is best to start with a rather low degree of relief, which may be raised easily, if required, by soaking in warmer water, while a relief once too high can be reduced only with difficulty. Should soaking in warm water at a temperature of 95° F. (35° C.) be insufficient to produce the desired degree of relief, the print may be immersed in a 1% solution of sodium carbonate as recommended by E. Guttmann. As a rule, however, this method should be used only as the last resort.

Pigmenting.—The brushes employed for applying the pigment are especially made for the process and may be obtained from dealers. They are made of fitch hair and the end is cut at an angle as shown in Fig. 344. To begin with, three brushes will serve, numbers 10 and 14 and a smaller one for detail work. As the worker progresses, additional brushes will be found convenient in order that a fresh brush may be used when it is necessary to apply pigments of different consistency to any part of the print.

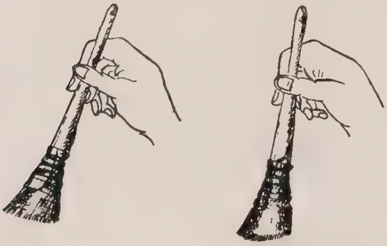

FIG. 344. Brushes and Methods of Holding the Brush in the Pigmenting of Bromoils.

Brushes should be kept in good condition, not only because they are expensive, but because the quality of the work depends to a large extent upon their condition. After use, the brush should be thoroughly cleaned with gasoline, carbona, or a similar solvent and washed in soap and water until free of both solvent and pigment. Take care not to get the brushes out of shape while cleaning, and when they are thoroughly cleaned, wrap in a piece of white paper and place a rubber band around the handle in order to keep the brush in its proper shape.

The pigments used are similar to those used in lithography and may be obtained from dealers in photo supplies.

It is necessary to keep the print wet from underneath during pigmenting and for this a pigmenting pad is used. Pads are a commercial article and may be obtained from any of the dealers carrying oil materials or one may be improvised from a sheet of glass and four or five sheets of blotting paper. Soak each sheet of blotting paper in water until thoroughly wet and then place on top of one another upon the glass plate. Upon this spread one or two thicknesses of muslin or cheesecloth. Then remove the print from the wash water and place on top of the pad. With a blotter or piece of silk take off the excess moisture, being careful not to make the surface wholly dry. Only take off the excess water. It will be noticed that the image stands out in relief and the appearance of the print at this stage is a good indication of the way it will take the pigment. The greater the relief the more readily the ink will take.

Squeeze out a very small quantity of pigment on the palette. Only a small quantity is needed, as a piece the size of a pea will do for several 8 × 10 prints. Instead of a palette the glass side of an old negative may be used. Spread the pigment out in a thin layer with the palette knife and tap the brush on the same so as to take up the pigment on the end of the hairs. When the brush has become charged with the pigment, work it around on a clear portion of the glass in order to distribute the pigment evenly. It is well to prepare pigments of two consistencies at the beginning, since it is rare that the same pigment can be used throughout the operation owing to the fact that some parts of the image require a softer pigment in order to make the pigment adhere. Either linseed oil, Robertson's medium or megilip may be used to soften the hard ink. Only a trace of any one of these is necessary to completely change the ink and, therefore, they should be added with caution.

The method in which the brush is used to apply the pigment varies greatly with different workers. Some have a pressing, smudging action, while others simply dab the brush on the surface. It is difficult to give any precise directions on this point and with practice one will develop a distinctive method of his own.

It is well to begin pigmenting with the ink as it comes from the tube and continue until the image is distinct and the shadows well defined when it may be desirable to change to a softer pigment. It is easy to tell when more pigment is needed, for the brush will begin to pick up the pigment instead of depositing it.

To lighten any portions which have been over-pigmented, the operation known as hopping is used. In this, the brush is held vertically and allowed to drop upon the surface from which the pigment is to be removed. Wire holders are supplied to hold the brush so that hopping may be carried on without fatigue.

Do not be afraid to apply plenty of pigment, but do not try to put it all on at once. Smooth it down to an even tint on the palette and take up a little on the brush at a time. When this is exhausted, take up more. A smooth, even tone will result if plenty of pigment is used and thoroughly worked into the surface. If the pigment is not well worked in, the print will be weak and "gritty" and the tone will be impure.

All detail which is to appear in the finished print should be apparent after the first inking. If parts of the image are inked strongly before the desired details appear, it is difficult to ink these later.

Particular care is necessary, especially in the case of large prints, or where a long time is required for pigmenting to keep the paper thoroughly wet. To this end it is well to soak the print in water frequently during pigmenting.[22]

Troubles in Pigmenting.—

Highlight areas repell soft ink.

Excessively swollen prints. There is no remedy.

Print refuses to accept ink.

Paper is not suitable for the process, bleaching solution incorrectly prepared. There is no remedy.

Print inks up as a negative.

The ink is too soft. Clean up and apply harder ink.

Print accepts ink but more or less evenly.

Insufficient swelling. Use a warmer water bath for soaking.

Spots appear attracting more ink than the surrounding areas.

Insufficient swelling in spots due to air bubbles or fault of bleaching from the presence of hypo in the bromide print.

Small white spots which refuse to take the ink.

Drops of water on the surface. If the spots move with the brush, the water is on the brush.[23]

Bromoil Transfer.—Bromoil transfer, as its name indicates, consists in transferring the pigment from the bromoil print to a piece of plain paper. As the oily pigment lies on top of a more or less tanned and swollen gelatin it will leave the bromoil print and adhere to a piece of moist paper when the two are brought together under pressure. Transfers, accordingly, have a distinctive appearance which is unlike other pigment processes since in these the image forming pigment is either incorporated in or lies over a colloid layer, while in transfer the pigment lies on a plain uncoated paper.

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[22] Grimwood, *Brit. J. Phot.* **72** (1925) 320. Usher, *Brit. J. Phot.* **75** (1927) 191. Fiedler, *Photofreunde*, **4** (1924) 13. Namias, *Brit. J. Phot.* **61** (1914) 626. Gabriel, *Brit. J. Phot.* **76** (1929) 543, 559.

[23] Mayer, *Amer. Phot.* **19** (1925) 506.

Preparation of the Bromoil for Transfer.—Any bromide paper which is suitable for the bromoil process may be used for the bromoil prints from which a transfer is to be made.

Bromide papers having a super coating (that is, a second gelatin layer to protect the emulsion and prevent abrasion markings) may be used under certain conditions.[24]

To obtain a transfer of good quality soft ink must be used in pigmenting the bromoil as it is impossible to transfer hard ink with certainty, owing to the tenacity with which it adheres to the original bromoil. Soft ink, however, cannot be used unless a high relief is obtained or the ink will adhere to the highlights of the bromoil and a print of the proper gradation cannot be obtained. Consequently it is necessary to start with a rather high relief; this fact must be borne in mind when the print is being made ready for pigmenting and the temperature of the water in which the swelling takes place regulated accordingly. The use of a high temperature, however, may cause the gelatin in the highlights to soften to such an extent that it pulls off in pigmenting or in transfer. When this occurs it is well to make use of ammonia as previously described. As the ink is more easily transferred from the highlights than from the shadows, in consequence of the greater relief of the former and the fact that owing to the tanning of the gelatin the pigment in the shadows is more strongly retained than in the highlights, the contrast of the transfer is usually much less than that of the bromoil. In pigmenting, therefore, the bromoil is made considerably more contrasty than would be required where it to be left as it is. Owing to the fact that the transfer of ink in the shadows may not be complete, it is the practice of many workers to considerably over ink such portions in order that the transfer may have the proper depth in the shadows. To reach the same end other workers have recourse to multiple transfer; the first bromoil being inked normally and transferred, then reinked, paying especial attention to the shadows.

Transfer Papers.—The best papers for transfer are those used for copper plate printing, but water color and drawing papers of good quality are suitable as a rule. Very rough or absorbent papers may require sizing to keep the pigment on the surface of the paper. A 2% solution of arrowroot may be used for this purpose.

As a general rule, the transfer paper should be used dry. Some few papers, however, must be slightly damp. In this case two sheets of blotting paper should be thoroughly and evenly dampened and the sheet of transfer paper placed between them, under slight pressure, for several minutes. As different papers require different treatment, one should use a particular paper until thoroughly familiar with its characteristics.

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[24] Symes, *Brit. J. Phot.* **70** (1923) 103.

As a general rule, the more absorbent the paper the better the transfer of pigment. If the paper is too wet the pigment transfers with difficulty, or not at all, and the transfer is smeary. The proper condition is very important and must be learned by experience.

Transfer of the Pigment Image.—A number of presses, similar to those used by copper plate printers, are available commercially.[25]

The primary requirements of a satisfactory press are two in number: (1) The pressure on the rolls must be absolutely even and capable of regulation by the operator, and (2) one must be able to examine the condition of the transfer at any time without danger of shifting the position of the bromoil or the transfer.

As soon as pigmenting is complete the bromoil is ready for the transfer. For this purpose we require, in addition to a suitable press, two sheets of blotting paper, three sheets of thick, hard, glazed pasteboard and a pad of felt—all of which should be at least double the length of the bromoil print. On one of the sheets of pasteboard is placed one of the sheets of blotting paper and on this the pigmented bromoil, face up. Over this is placed the transfer paper, and over this another sheet of blotting paper. These two sheets of blotting paper serve the purpose of absorbing the moisture squeezed from the bromoil print which might otherwise cause trouble. Finally a sheet of pasteboard is placed over the blotting paper, then over this the felt pad and lastly another sheet of pasteboard.

The entire pack is now inserted between the rollers and carried through once with a uniform motion and with but slight pressure. The pressure is then increased slightly and the pack carried back through the press in the opposite direction. Then the top of the press pack is removed, the cover of the transfer paper raised and the appearance of the transfer examined. If the transfer of ink is only slight, the press pack is replaced and carried through the press again with increased pressure. Then if the shadows still lack intensity registration marks should be made, the bromoil print removed, resoaked in water and the shadows pigmented after which the bromoil is placed on the transfer paper, its position registered, and again passed through the press. The pressure should not in any case be so great that the rolls can be started only by a decided effort; they must always move easily and smoothly. Repeated slow passage of the press pack through moderately tightened rollers is always more advantageous than a single passage under very heavy pressure. With heavy pressure there is likewise the danger of destroying the bromoil, as the gelatin film in its swollen condition may adhere to the transfer paper. This trouble, however, is occasionally met with when using some papers with only a moderate amount of pressure.

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[25] As for example, those of the Autotype Company, Sinclair, Drem, and Partington. See also: Prett, *Brit. J. Phot.* **70** (1923) 300. Santeul, *Brit. J. Phot.* **70** (1923) 301.

Methods of Transfer Without a Press.—If the transfer paper is dampened with a solvent of the oil pigment such as benzene, benzol, or turpentine, only light pressure is required to transfer the pigment from the bromoil to the transfer paper, since the transfer is effected by the action of the solvent and the adhesive power of the paper. Even the light pressure obtainable in a printing frame or light rolling with a print roller is often sufficient.[26]

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[26] Zaepernick, H., *Amer. Phot.* **18** (1924) 732.

CHAPTER XXVI

PRINTING PROCESSES: PLATINOTYPE, IRON AND PLAN-COPYING PROCESSES

Printing Processes Based on Iron Salts.—A number of the organic salts of iron are sensitive to light and a still larger number are sensitive in the presence of organic matter. Several printing processes are based upon the light sensitive iron salts, among them, ferroprussiate (blue print), cyanotype (blue lines on a white background), kallitype, platinotype, and a number of other processes which are now obsolete.

The Platinotype Process.—The Platinotype Process results in an image of pure metallic platinum. As platinum is one of the most stable metals, prints made by the Platinotype Process may be regarded as being as permanent as the paper on which they are made. The pure black image of finely divided particles of platinum has a certain intrinsic quality which is unique and it is very properly regarded as one of the finest processes of photographic printing.

Although some of the salts of platinum are sensitive to light, particularly in the presence of organic matter, the Platinotype Process is an indirect one depending upon the reduction of a ferric salt to the ferrous which, upon being dissolved in an alkaline oxalate, such as potassium oxalate, reduces the platinum salt (potassium chloroplatinite) to the metallic state.[1]

$$Fe_2(C_2O_4)_3 + \text{light} \rightarrow 2Fe(C_2O_4) + 2CO_2,$$

$$6FeC_2O_4 + 3K_2PtCl_4 \rightarrow 2Fe_2(C_2O_4)_3 + Fe_2Cl_6 + 6KCl + 3Pt.$$

Papers for the Platinotype Process.—Platinum paper, unfortunately, is no longer an article of commerce; sensitizing, however, is not particularly difficult. A good quality, matt drawing paper free from iron and other metallic impurities, is suitable and should first be "sized" by immersion for 10 to 20 minutes in a 3% solution of arrowroot, which has been boiled and filtered before use. Upon removal from the arrowroot solution, the paper is hung on a line and allowed to dry slowly without heat.

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[1] Sheppard, *Photography as a Scientific Implement,* p. 170.

The sensitizing solution is prepared in three stock solutions as follows:[2]

A.	Potassium chloroplatinite	166.6 gm.	727.8 gr.
	Water to	1000 cc.	10 oz.
B.	Ferrous oxalate	220 gm.	962.5 gr.
	Water	1000 cc.	10 oz.
C.	Ferrous oxalate	220 gm.	962.5 gr.
	Potassium chlorate	4.45 gm.	21.5 gr.
	Water to	1000 cc.	10 oz.
	For normal negatives: *A*	50 cc.	6¼ fl. oz.
	B	30 cc.	3¾ fl. oz.
	C	20 cc.	2½ fl. oz.
	Water	40 cc.	5 fl. oz.
	For contrasty negatives:		
	A	50 cc.	6¼ fl. oz.
	B	50 cc.	6¼ fl. oz.
	C	——	

The sheets of sized paper may be laid on clean glass or in the bottom of a white enamel tray and the sensitizing solution applied with a soft camel's hair brush. After sensitizing, the paper should be dried as quickly as possible, in a dry atmosphere. As the paper is extremely sensitive to moisture, when thoroughly dry it should be transferred immediately to an air-tight container. A small quantity of calcium chloride should be placed in the storage box to absorb any moisture still remaining. The paper should not be removed from the container until it is to be placed in the printing frame.

The exposure scale is rather longer than that of developing papers; the best results are obtained with a rather brilliant negative possessing somewhat greater contrast than would be considered necessary for developing papers. Clear and brilliant shadow gradation is particularly important.

Exposure.—The paper should be handled only in artificial or very subdued daylight. The negative should be thoroughly dry. When printing by daylight, it is well to place a sheet of wax paper or cellophane over the back to protect the paper from moisture. The image appears as an orange-brown deposit against the yellow surface of the paper. Experience is required to determine the proper exposure from the appearance of the partially visible image, but generally the exposure is sufficient if full detail can be seen in the shadow portions of the image.

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[2] Hubl, *Platindruck;* Knapp, Halle a/s.

Development.—The developer is prepared as follows:

Neutral potassium oxalate	300 gm.	1312 gr.
Oxalic acid	5 gm.	21.9 gr.
Water to	1000 cc.	10.0 oz.

For use it is heated to a temperature of 125° to 180° F. (52° to 82° C.). The addition of small amounts of potassium bichromate will increase contrast while the addition of dilute hydrochloric acid will result in softer prints. Warmer tones may be obtained by the addition of mercuric chloride. The amount required in each case must be determined by trial.

Since the image appears almost immediately, the paper must be immersed in the solution in such a manner that it is easily and quickly covered in one sweep. Any air bubbles which appear should be carefully removed with a soft brush or the tip of the finger. With correct exposure, there is no fear of overdevelopment, and after a full minute's immersion, the print may be removed and immersed in the clearing bath composed of hydrochloric acid 1 oz., water 50 oz. (20 to 1000 cc.).

After 5 minutes' immersion in this bath, the print should be transferred to a second bath of similar composition for 5 minutes and then to a third for another 5 minutes, after which it is washed for 15 or 20 minutes in running water and dried.

Platinum Printing (Clerc's Process).—L. P. Clerc has given details [3] of a process in which the paper is sensitized with the iron salts alone and the platinum compound added to the developer.

The paper is first sized by immersion in a solution containing 8 grams of gelatin and 2 grams of potassium alum in 1000 cc. of water used at a temperature of about 125° F. (52° C.). When dry, the sized paper is coated with

Ferric oxalate	25 gm.	109.4 gr.
Oxalic acid	2 gm.	8.8 gr.
Lead oxalate	1 gm.	4.4 gr.
Distilled water (hot)	1000 cc.	10.0 oz.

using a soft, camel's hair brush. After coating, the paper should be dried as quickly as possible, avoiding, however, the use of undue heat and, if it is not to be used at once, placed in an air-tight container.

As the image is barely visible, it is not strictly a printing-out paper and the best procedure is to expose by time exactly as with a developing-out paper. Therefore, except when steady sunlight is available, artificial light, such as the electric arc, mercury vapor lamps, ultra-violet sun lamps or photoflood lamps, is to be preferred because of its greater constancy.

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[3] Clerc, *Photography, Theory and Practice,* Pitman.

The developing solution is prepared as follows:

Potassium oxalate (neutral)	200 gm.	875 gr.
Di-sodium phosphate	50 gm.	220 gr.
Water to	1000 cc.	10 oz.

For use, add to each 100 cc. of the above, 10 cc. of a 10% solution of potassium chhloroplatinite. The developer is applied with a flat camel's hair brush. When fully developed, the print is cleared in dilute hydrochloric acid and washed in the usual way.[4]

Palladium Printing.—As a metal palladium is very similar to platinum and palladium printing likewise is very similar to platinum printing. Palladium, however, is much cheaper and the color of the image is a warm black while that of platinum is a pure black.[5]

Any good drawing paper, such as Whatman's cold pressed, Michallet charcoal, Strathmore or a good linen bond stock may be used. The less absorbent the paper, the greater the brilliancy and contrast of the print. Sizing is not required except on very porous papers or when brilliant prints are required. When sizing is necessary, the arrowroot formula on p. 692 may be used.

The following formula is suggested for sensitizing.

1.	Ferric oxalate	26.6 gm.	1163.2 gr.
	Oxalic acid	1.83 gm.	80.0 gr.
	Water to (distilled)	100.0 cc.	10.0 oz.
2.	Ferric oxalate	26.6 gm.	1163.2 gr.
	Oxalic acid	1.83 gm.	80.0 gr.
	Potassium chlorate	.5 gm.	30.0 gr.
	Water (distilled) to	100.0 cc.	10.0 oz.

[4] A silver-platinum paper was issued commercially under the trade name *Satista* by the Platinotype Company of England. For details of the preparation of the paper and its manipulation, see *Brit. J. Phot.* **61** (1914) 777 or B.P. 20,022 of 1913 issued to William Willis.

[5] Warm black and sepia prints are obtainable with the platinum process by the addition of mercuric chloride to the developer.

ANDERSON—Palladium vs. Silver for Photographic Prints. Phot. Tech. **2** (1940) Aug. p. 58.

ANDERSON—The Technique of Pictorial Photography.

ANDERSON—Hand-Sensitized Palladium Paper. Amer. Phot. **32** (1938) 457.

3. Sodium chloropalladite	15.0 gm.	65.6 gr.
Water (distilled) to	100.0 cc.	10.0 oz.

For prints from average negatives:

1. 14 parts
2. 8 parts
3. 24 parts

For prints of greater contrast:

1. — parts
2. 22 parts
3. 24 parts

The sensitizing solution is applied with soft camel's hair brush which should have no exposed metal parts. The solution spreads easily; in general, no difficulty is experienced in obtaining a coating of the necessary uniformity. When coated, the paper is hung up to dry in a dark place. Drying may be hastened by an electric fan or moderate heat. The use of heat is advisable in damp weather. If not for use immediately, the coated paper should be stored in an airtight container with a small quantity of dry calcium carbonate to absorb any moisture present in the sealed container.

Exposure and Development.—Palladium is strictly a printing-out process and requires sunlight or an intense source of artificial light, such as the carbon arc, mercury lamps, ultra-violet sun lamps or Photoflood lamps. As the image is only slightly visible, it is best to expose by time as when using a developing-out paper.

Development should follow the exposure immediately as the paper readily absorbs moisture and the absorbed moisture results in a loss in brilliancy. The developing solution is prepared as follows:

Potassium oxalate	500 gm.	16 oz.
Water (hot)	1500 cc.	48 oz.

Warmer tones may be obtained by adding mercuric chloride.

Use at room temperature in a glass or porcelain tray. Development requires about three minutes but longer immersion does not harm, as development proceeds to completion and then stops. The developing solution may be used over and over, fresh solution being added from time to time.

After development, the print is cleared by immersion for five minutes in each of three baths of dilute hydrochloric acid; washed and dried face up on a blotter.

The Ferroprussiate Process.—This, the familiar blueprint process, is used chiefly for making copies of architects' and machine plans. The relatively short scale of gradation does not lend itself well to ordinary subjects. The paper is coated with ferric ammonium citrate and potassium ferricyanide. The ferric salt is reduced to the ferrous upon exposure and, when the print is placed in water, ferro-ferricyanide, or Berlin Blue, is formed as a result of the reaction between the ferrous salt and the ferricyanide.

Blueprint paper is obtainable commercially in a number of different speeds. The paper is extremely sensitive to moisture and should be kept in tightly sealed cans. The paper is exposed either to daylight or to a suitable source of artificial light such as the mercury vapor lamp in frames especially designed for the purpose. Most commercial printing, however, is done with continuous machines of which there are a number of makes. In general, the principle employed is as follows: An endless belt carries the tracing to be printed and a band of paper around a glass surface formed in the shape of a half-cylinder. This cylinder is illuminated from the inside usually with a mercury vapor tube. The paper is washed by jets of water in the same machine and dried between cloth belts passing over a heated drum.

The paper is exposed until the lines of the drawing appear yellow on a bluish-green background. Development is effected by placing the print in a stream of running water for 5 to 10 minutes. Alkaline water should not be used as it results in bleaching of the print.

Prints are usually hung on a line to dry but may be placed on blotters or cloth if the surface moisture is first removed to prevent drying marks from drops of water on the surface.

Preparation of Blueprint Paper.—Almost any paper stock may be used except those consisting wholly or in a large part of wood pulp. In general, a smooth matt paper, well sized, is preferable.

A satisfactory means of coating small quantities of paper is to attach a sheet of paper to a board using stainless steel pins and apply the sensitizing solution with a large, flat, rubber-bound brush. A metal-bound brush must not be used. The paper should be coated as evenly

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WALL—The Iron Salts. A Summary of Iron Printing Methods. Amer. Phot. **16** (1922) 677, 766; **17** (1923) 4.

STENGER—The Blueprint as a Photographic Copying Process. Phot. Ind. **30** (1932) 461, 487, 409, 525.

HARPER AND POWELL—Photographic Ferro-Prussiate Processes. B.P. 461,893 of 22/8/35. Addn. to B.P. 427,746.

and as quickly as possible, going over the surface with a charged brush, first in one direction and then in rapid circular strokes.

Rapid drying is essential. Either an electric fan or a hot-air dryer such as used by hairdressers may be employed. Paper which is allowed to dry under ordinary room conditions possesses poor keeping qualities.

Herschell's formula is the simplest and is still unsurpassed for a deep rich blue but is much slower than the two other formulas shown.[6]

The sensitiveness of the paper may be increased by increasing the ferric ammonium oxalate and the ferric sodium oxalate, but the whites are likely to be blue-tinged. The addition of a small quantity of potassium bichromate—50 gr. to the gallon (0.9 gm. to 1000 cc.)—improves the keeping properties, but lowers the sensitivity.[7]

Cyanotype or Positive Blueprint Process.—This process produces blue lines on a white ground from an ordinary drawing on tracing cloth or paper. The paper is coated with a solution containing ferric chloride and tartaric acid. The ferric salt is reduced to the ferrous upon exposure to light. The application of potassium ferrocyanide as a developer results in the ferrous salt being converted into ferric-ferrocyanide or Berlin Blue. The product resulting from the reaction of the ferric salt and potassium ferrocyanide is colorless and as it is soluble in water, is removed by washing, producing an image of blue lines on a white background or a positive from a positive drawing. It will be observed that the reaction taking place is practically the reverse of that in the ordinary blueprint process.[8]

Positive blueprint paper is available commercially, but is not widely used owing to its poor keeping qualities.

The paper is exposed in the same manner as ordinary blueprint paper until the lines are distinctly visible in a clear yellow color on a bluish-green background.

A 20% solution of potassium ferrocyanide is used for development. As it is essential that none of the developer reach the back of the print, the paper is pinned to a board using pins of stainless steel and the developer applied with a broad rubber-bound brush. Development is

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[6] Willcock, *Brit. J. Phot.* **82** (1935) 456.

[7] Preparation of plant copying papers utilizing iron compounds: U.S.P. 1,877,246 Kivich; U.S.P. 2,126,504 Holden; U.S.P. 2,137,015 Crowley and Goodyear; U.S.P. 2,093,738 Reynolds; B.P. 416,489 Murray and Spencer; B.P. 418,369, 420,900, 442,863, 491,586, 494,572 Holden; B.P. 461,893 Harper; B.P. 462,554 Norman and Mason. Review of Copying Processes. *Phot.Tech.* **I** (1939) Nov. p. 38.

[8] Collet, B.P. 4632 of 1877.

	Herschel		Rapid		Ultra Rapid	
1. Ferric ammonium citrate	800 gm.	8 oz.	600 gm.	6 oz.	350 gm.	3½ oz.
Water to	1 liter	10 oz.	1 liter	10 oz.	1 liter	10 oz.
2. Ferric ammonium oxalate	——	——			187.5 gm.	1.875 oz.
Water to	——	——			1 liter	10 oz.
3. Ferric ammonium oxalate	——	——	200 gm.	2 oz.	300 gm.	3 oz.
Water to	——	——	1 liter	10 oz.	1 liter	10 oz.
4. Ferric oxalate	——	——	12.5 gm.	⅛ oz.	50 gm.	½ oz.
5. Potassium ferricyanide	400 gm.	4 oz.	200 gm.	2 oz.	187.5 gm.	1.875 oz.
Water to	1 liter	10 oz.	1 liter	10 oz.	1 liter	10 oz.
6. Gum arabic	150 gm.	1.5 oz.	150 gm.	1.5 oz.	150 gm.	1½ oz.
Water to	1 liter	10 oz.	1 liter	10 oz.	1 liter	10 oz.
Water to make	8 liters	80 oz.	8 liters	80 oz.	8 liters	80 oz.

(All solutions should be mixed in the order shown in the formula.)

The ferric oxalate is sparingly soluble in water and should be added in the dry state.

rapid, requiring about one minute. Cold water should then be sprayed over the surface of the print to remove the surplus ferrocyanide. After a preliminary washing of three to four minutes, the print is placed in a 10% solution of hydrochloric acid for 1 or 2 minutes, then transferred to a second bath of the same composition, where it may be allowed to remain for 4 to 5 minutes and is then washed for several minutes in running water and dried.

Preparation of Cyanotype Paper.—The following formula is suitable:

Solution A			
Gum arabic	170 gm.	6 oz.	
Water	630 cc.	23 oz.	
Solution B			
Tartaric acid	40 gm.	617 gr.	
Water	150 cc.	5 oz.	135 min.
Solution C			
Ferric chloride solution Specific gravity 1.453	113 cc.	4 oz.	

Distilled water should be used in preparing these solutions. When mixing the sensitizing solution, the acid solution is added to the gum solution, and the ferric chloride added last. The mixture should be allowed to stand 24 hours and then diluted with water to a specific gravity of 1.0.

The paper is coated in the same manner as ordinary blueprint papers.

The Vandyke Process.—This process is used chiefly for making copies of tracing plans to be used subsequently as a negative for blueprinting. It produces white lines on a brownish-black background. The paper is coated with a light sensitive iron salt and silver nitrate in a solution of gelatin. Upon exposure to light, the ferric salt is reduced to the ferrous which in turn reduces the silver nitrate to metallic silver when the print is placed in water. Some of the silver nitrate is reduced to silver by the exposure, but this is a secondary factor in the formation of the image.[9]

Papers of this type are obtainable commercially in various grades. Sensitized cloth is also available.

The paper is exposed to daylight, or a strong source of artificial light, in the same way as blueprint paper. The image appears as white lines on a light brown ground. After the exposure, the print is washed in running water 1 or 2 minutes and then placed in a 2% solution of hypo. Fixing requires about 5 minutes, after which the print is washed for 10 to 15 minutes and dried.

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[9] Arndt and Troost, D.R.P. 6317 of 1894.

The following is a suitable sensitizer for preparing paper of this type:

Solution A

Ammonio citrate of iron, green	175 gm.	1344 gr.
Water	1000 cc.	16 oz.

Solution B

Gelatin	30 gm.	230 gr.
Water	500 cc.	8 oz.

Solution C

Silver nitrate	50 gm.	385 gr.
Water	500 cc.	8 oz.

Soak the gelatin in water for 15 minutes and then dissolve by heat at 45° C. (100° F.), filter and add A. Then add B but do not stir. Keep the solution warm while sensitizing the paper.

The sensitizer is applied in the same way as when sensitizing blueprint paper and it should be dried rapidly, although not at so high temperature as ferroprussiate or cyanotype paper.

Kallitype.—Unlike the processes described previously, the uses of which are restricted to the reproduction of plans and sketches, Kallitype is suitable for subjects of a pictorial nature.

There are two methods of working the process; in the first, the paper is coated with a ferric salt, usually the oxalate, and silver nitrate. Upon the exposure to light, the ferric salt is reduced to the ferrous, and upon development in a solution containing borax and rochelle salt, the silver nitrate is reduced to metallic silver. The second method consists in the use of the iron salt alone as a sensitizer, followed by development in a solution of silver nitrate.

The formulas which follow are due to James Thomson.[10]

[10] *Amer. Phot.* 17 (1923) 442.

Thomson—Possible Substitutes for the Platinum Print. Amer. Phot. **11** (1917) 642.

Thomson—Kallitype. Amer. Phot. **17** (1923) 422.

Valenta—Kallitype (an excellent summary of previously published papers on the subject). Bibliography. Das. Atelier **27** (1920) 10.

Citrate of iron and ammonia (brown)	73.4 gm.	32 gr.
Ferric oxalate	36.6 gm.	16 gr.
Potassium oxalate	75.4 gm.	33 gr.
Copper chloride	9.15 gm.	4 gr.
Citric acid	9.15 gm.	4 gr.
Silver nitrate	22.9 gm.	10 gr.
Oxalic acid	22.9 gm.	10 gr.
Gum arabic	22.9 gm.	10 gr.
Distilled water to make	1000 cc.	1 oz.

Potassium bichromate solution (20 grains to the ounce or 45.7 gm. to 1000 cc.) as required.

From 5 to 10 drops of the latter to each ounce of the sensitizing solution is the normal quantity but where greater contrast is desired, the amount should be increased.

After mixing, the solution should be stored in a dark place for 24 hours. Before sensitizing, it should be filtered through cotton.

Any good linen paper will serve if given a preliminary sizing. Either arrowroot or gelatin may be used for this purpose. Gelatin is perhaps the simpler. The following formula is suitable:

Gelatin	11.43 gm.	50 gr.
Powdered alum	6.86 gm.	30 gr.
Water to make	1.0 liter	10 oz.

First allow the gelatin to swell in cold water and then with constant stirring add it and the alum to the remainder of the water and bring to the boiling point. The sizing solution may be applied with a broad flat brush or with a cloth pad. After coating, the sheets are suspended from one corner in a warm room and allowed to dry normally.

The sensitizing solution is applied with a flat camel's hair, rubber-set brush, and the paper is dried as rapidly as possible, using a moderate amount of heat.

Either daylight or a strong source of artificial light may be used for printing. The image is faintly visible and of a tawny hue. Usually only the shadows and some of the half tones will be visible when the paper is properly exposed.

The developer is as follows:

Silver nitrate	91.5 gm.	40 gr.
Citric acid	22.9 gm.	10 gr.
Oxalic acid	22.9 gm.	10 gr.
Distilled water	1000 cc.	1 oz.
For blue-black tones add sodium phosphate	4 gm.	2 gr.

For use, take one part of stock solution to seven parts of water. Greater contrast may be obtained by using a more concentrated developer.

Immerse the print face down and turn over immediately to break bubbles which, if permitted to remain, will result in white spots. Allow the print to remain in the developing solution for one minute, rinse well and fix for 5 to 10 minutes in a plain solution of hypo as follows:

Hypo	3.4 gm.	15 gr.
Water	1000 cc.	10 oz.

Finally, wash for 15 to 20 minutes in running water.

Diazo Processes.—A large number of processes based upon the sensitiveness of diazo compounds have been patented, but only a few papers of this type have actually been placed upon the market. The papers available are designed for making copies of tracings and drawings and for this purpose are tending to supplant the blueprint processes.

The fundamental reaction in these processes is the formation of a colored azo compound from the reaction between a phenolic or amino compound and a diazo compound. This reaction, which is termed *coupling*, takes place most readily with phenolic compounds in the presence of an alkali and with amino compounds in a neutral or slightly acid state. Most diazo compounds are sensitive to light; once decomposed, they are unable to couple with an azo dye component and cannot, therefore, be converted into a colored dyestuff.[11] Four types of diazo papers are possible:[12]

1. Diazo compound A decomposed by light to B; developed by the application of a coupler C in alkaline solution which reacts to give a colored product with A but not with B.[13]

2. Diazo compound A and coupler C coated together but prevented from reacting by the presence of an organic acid. Such papers are developed by bathing in a weak alkali; or, by exposing to ammonia vapor.[14]

3. Diazo compounds A and C coated together but with the latter compound modified by the formation of additional compounds in such a manner that it will not couple in a neutral condition, development being

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[11] Murray, *Phot. J.* **63** (1933) 6 (Suppl.).

[12] Spencer, *Phot. J.* **58** (1928) 490.

[13] Green, Cross and Bevan, G.P. 56,606 of 1890; *Brit. J. Phot.* **37** (1890) 637.

[14] Koegel and Neuenhaus, G.P. 376,385, 386,433; B.P. 234,818 of 1926; B.P. 210,862 of 1924.

effected by breaking up the addition compound by ammonia vapor, heat or the like.

4. Diazo compound A which is decomposed by light into compound D capable of coupling with unchanged A on standing, or on making the paper alkaline.[15]

In the Ozalid paper of Kalle and Company, which is based upon the patents of Koegel and Neuenhaus, the paper is coated with a diazo anhydride which does not couple directly with an azo component in a neutral condition but takes place readily in an alkaline condition.

The paper is first exposed to light beneath the tracing, the exposed portions bleaching while the unexposed portions retain the color of the diazo compound with which the paper is coated. The image is then exposed to ammonia vapor which converts the unexposed portions to a dye image the color of which depends upon the diazo compounds with which the paper is coated. At the present time brown, black, blue line papers are available. No fixing or washing is required; hence distortion due to the shrinkage or expansion of the paper is eliminated and measurements and computations may be made from the print with the assurance that it is an accurate copy of the original tracing.

[15] Feer, G.P. 53,455 of 1889; Eder's *Jahrbuch* **5** (1891) 529.

Murray—Diazo Compounds in Photography. Phot. J. **73** (1933) (Suppl.) 6.

Sedlaczek—Diazotype. Phot. Ind. **33** (1935), 1062, 1064, 1082, 1084, 1108.

Seyewetz and Mounier—Action of Light on Diazonium Compounds and Azo Dyes. Bull. Soc. Chim. Fr. **43** (1928) 827; Sci. et Ind. Phot. **8** (1928) 231.

Spencer—Photographic Applications of Diazo Compounds. Phot. J. **68** (1928) 490.

CHAPTER XXVII

FINISHING AND MOUNTING THE PRINT

Methods of Finishing Photographs.—In artistic hands, the application of a pigment of suitable color, which for black prints may be compounded of lamp black and Payne's gray, may be used to good advantage to build up shadow areas which lack depth, or to darken halftone areas. The print should first be uniformly covered with medium, sometimes known as megilip, the pigment reduced to the proper consistency by dilution with the thinning medium using a clean glass plate and a pallette knife and, after having been spread out in a thin layer on the glass, is applied to the print with a circular rubbing motion using a tuft of absorbent cotton. The pigment may be removed from small details, which should not be darkened, with a wisp of cotton about the end of a match dipped in the thinning medium. If a mistake is made, the pigment may be removed entirely with a soft cloth moistened with turpentine.

The finishing of prints with pastel crayons is not as popular as in years past, but a modification, known as the abrasion process, developed by Mortensen,[1] has been used by him and his students with great success.

The airbrush finds widespread use in the retouching of photographs, especially for reproduction.[2]

Coloring or Tinting of Photographs.—Photographs may be colored, or tinted, with pastel, water or oil colors, however, the first mentioned is now little used.

Prints for coloring should be lighter than for ordinary requirements, as the depth of the image is increased by coloring. Semi-matt and matt surfaces are preferable. Glossy surfaces can be colored but are more difficult.

[1] Mortensen, *Print Finishing* (San Francisco 1939). Mortensen, *Popular Photography* **3** (1938) Aug., Sept., Oct., p. 20.

[2] Kadel, *Airbrush Art.* Stine and Frasier, *The Airbrush.* Shures, *Popular Photography* **3** (1938) Aug. p. 17.

JAMIESON—Pictorial (Retouching) Control and Material for Use Therein. U.S.P. 2,108,261, 1934.

When water colors are to be used, the print should first be soaked for at least one-half hour in water in order that the gelatin may swell and accept the color well. With some papers which have an extra-hardened, super-coating, it may be advisable to soak the print for 10 to 15 minutes in a weak (2 to 5%) solution of ammonia. When ready for coloring, place the print on a sheet of glass, or other smooth water-proof surface, and blot off the surface water with a viscose sponge or *lintless* blotting paper. Prepare much diluted solutions of the required colors and apply with sable or camel's hair brushes, blotting off the surplus solution after each application. Use only light washes of color, building up to the color required through successive applications. Concentrated colors, however, can be used for touching up small, brilliantly colored details. Mixed colors may be obtained either by mixing the colors in solution or by successive application of the colors to the print.

In coloring with oil, the transparent colors sold for coloring photographs should be used rather than the opaque pigment of the artist. The dry print should first be covered uniformly with medium using a tuft of absorbent cotton. The surplus is then removed with a clean piece of silk or absorbent cotton. The color is applied either with or without dilution with the thinner, depending upon the colors used and the effect desired, using tufts of cotton or pieces of silk, rubbing the pigment in well to obtain even distribution. If the color is found to be too strong, it may be rubbed down with a piece of clean cloth or absorbent cotton. Small areas may be colored by wisps of cotton wrapped around the end of a match. The color may be removed where it is not wanted by the application of the medium, or a cleaning solution, on a clean soft rag or, if the area is small, a sable brush dipped in the medium may be used. Mixed colors are obtained by rubbing in first one of the required colors and then the other, blending by repeated application until the desired admixture has been obtained.[3]

Prints tinted with oil should be given from 12 to 24 hours to dry before mounting. Dry mounting is recommended.

Print Trimming.—Many prints are greatly improved by judicious trimming to eliminate unnecessary or objectionable subject matter and improve the composition.

A convenient means of determining how a print should be trimmed is afforded by two L shaped pieces of cardboard or opalescent celluloid.

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[3] Tobias, The Art of Coloring Photographic Prints. American Photographic Pub. Co. (Boston).

These may be placed on the print so as to form a frame the size and proportions of which may be altered at will and the effect studied. When the best composition has been decided upon, light pencil lines may be placed on the print as a guide for trimming. (A china marking pencil may be used with gloss papers.)

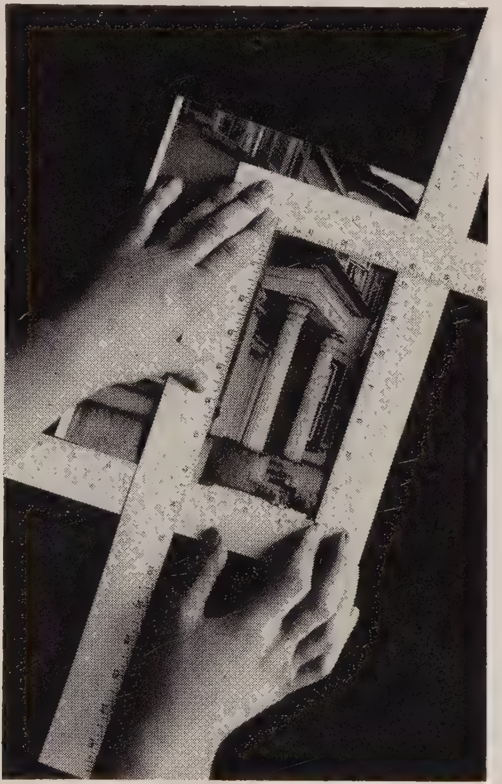

FIG. 345. Celluloid Squares Used in Determining the Proper Trimming of Prints.

If the print is to be mounted with paste, it may be trimmed at once; prints to be dry mounted, however, should not be trimmed until the mounting tissue has been attached in order that both may be cut to exactly the same size.

Prints are usually trimmed on a trimming board (Fig. 346). The print should be held firmly in place with the left hand to prevent slipping.

If a trimmer is not available or the print is larger than the blade of the trimmer, a straight edge and a sharp knife or a safety razor blade in a holder may be used. The print should be placed on a sheet of zinc, glass, wall board or heavy cardboard.

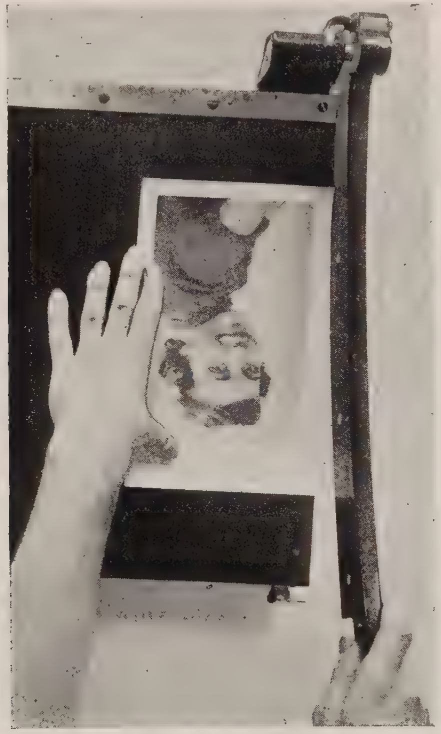

Fig. 346. Print Trimmer in Use.

Oval or circular prints are best trimmed with the aid of metal trimming guides, which may be obtained in various sizes from the larger dealers, and a swivel wheel cutter.

Mounting.—A print is not really complete until mounted. The function of the mount is to form a frame for the picture, a background which will separate it from its surroundings and display it more effectively. White or light mounts are preferred at the present time. A white mount, however, has the effect of increasing the apparent depth of the shadow portions of the print, especially if the margins are generous, and in such cases, it is usually desirable to make the transition from the picture to the mount less abrupt by double-mounting (p. 710), so that the picture is enclosed within a narrow gray or black frame. In general, this inner mount should be lighter than the darkest tones of the picture and darker than the highlights; if, however, the margin is a line, it may be a solid black.

The color of the mount is also important. A brown-black or sepia print, for example, will seldom appear to good advantage on a neutral gray or pure white. Usually it will appear to much better advantage on a warm gray, ivory or cream mount. On the other hand, a cold gray print does not appear to good advantage on a warm-colored mount.

Mounting materials having a distinct color are in disfavor and brightly colored papers are undesirable even for toned prints.

The size of the mount is largely a matter of personal opinion although for exhibition purposes there are certain sizes which are recognized by the leading salons as standard. In general, the smaller the print the larger the mount may be in proportion.

In placing the print on the mount, the usual practice with a vertical subject is to make the margins on the sides and top equal and that below the picture considerably wider. With a horizontal subject, the usual practice is to make the margins at the sides and below equal and that above the picture somewhat less.

Types of Mounts.—The types of mounts to be described in this chapter are:

1. *The line mount* which consists of a narrow pencil or ink line on the mount around the picture. (Fig. 347.)

2. *The lined slip-in mount.* This differs from the line mount in being in two pieces: (1) the front with a cut-out opening which frames the picture and on which the surrounding line is placed, and (2) the back to which the picture and the front piece is attached. (Fig. 348.)

3. *The plate-sunk or embossed mount.* In a plate-sunk or embossed mount, the center area occupied in part by the picture is depressed so as to produce the effect of a frame. The term "plate sunk" is derived from the depression produced by the plate when making a print from a copper plate etching. Frequently, photographic prints are made with wide margins and the paper sunk to produce the effect of an etching. (Fig. 349.)

4. *Double mounting.* A double mount is made by mounting the print first on a sheet of thin mounting stock which is then trimmed to leave a narrow margin and then attached to a larger sheet of heavy

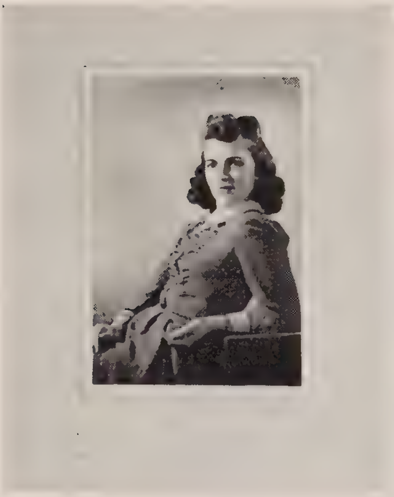

Fig. 347. Line Mount.

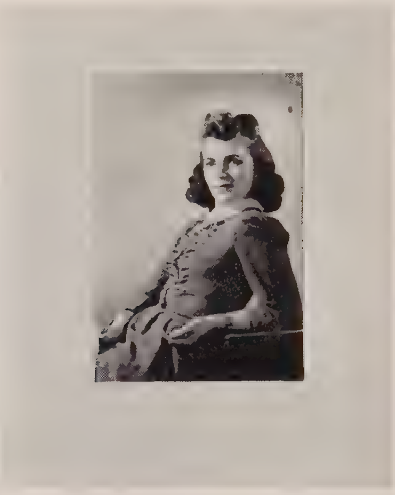

Fig. 348. Lined Slip-in Mount.

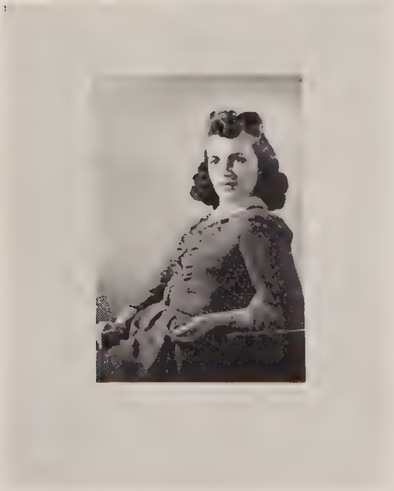

Fig. 349. Plate Sunk or Embossed Mount.

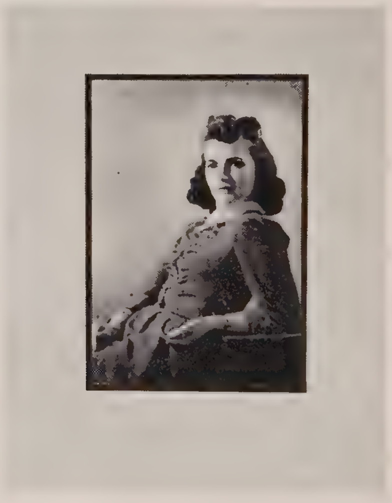

Fig. 350. Double Mount.

mounting stock. The contrast between the first and second mount gives added emphasis to the picture. In selecting papers for the two mounts it is usually desirable to avoid strong contrasts. The first, or inner, mount may be either lighter or darker than the other; in general, the greater the tone contrast between the two the greater the difference in the width of the margins. (Fig. 350.)

To prepare mounts, the following materials will be required:

Mounting papers.
Trimmer.
Sharp knife or safety razor blade in suitable holder.
Ruler.
Glue.
Pencil.
Black ink.

Papers suitable for mounting may be obtained from stationers, from printers by whom it is known as cover stock, and from artists' supply stores.

Preparing a Line Mount.—In preparing a line mount, the print is first mounted and then the line placed around the picture. After the print has been mounted, the position of the lines is decided upon. Two L-shaped pieces of cardboard may be used to advantage in determining the spacing which produces the best effect. The width of the margin is a matter of personal taste but in general, the sides and the top will be equal and the bottom somewhat greater.

Mark lightly in pencil the positions of the lines on the mount. Then cut a piece of cardboard the size of the area enclosed within the lines. Place this on the mount so that its edges coincide with the marked positions, and then draw the lines around the card, using a soft lead pencil and taking care to make the corners neat. In some cases, the appearance is improved by retracing the lines with a pencil freehand.

Making a Lined, Slip-In Mount.—The pieces of cardboard which are to form the front and back parts of the mount are first cut to the approximate size. The color and quality of the card stock used for the back are not important, as it is not seen. A piece of cardboard the size of the print is then cut and located on the cover of the mount in the position to be occupied by the picture. Draw a line around the card, and then with a straight edge and a sharp knife, or a safety razor blade in a holder, cut out the center portion cleanly.

Using the two L-shaped pieces of cardboard, determine the positions of the framing lines. Trace the lines lightly in pencil at first, then remove the cardboard guides and retrace the lines, using a straight edge.

The next step is to attach the front and rear portions of the mount. Apply a thin line of glue along the upper edge of the back portion, lay the upper half on it and place the two under pressure for several minutes.

Now apply a thin line of glue to the back of the print along the top and place the print in the proper position on the mount. Apply a thin line of glue along each of the three remaining sides of the mount and place under pressure for 10 to 15 minutes. Finally, trim the outside of the mount.

An attractive effect is produced by using either lighter or darker toned card stock for the front or cover portion of the mount, and making it a trifle smaller than the rear portion so as to produce a narrow contrasting margin to the mount. In this case, the cover portion must be trimmed to the proper size before being attached to the back portion.

Making a Plate Sunk or Embossed Mount.—Mounting stock of suitable color and surface and not over 1/32 inch thick, is first cut to the approximate size. The positions of the print and the embossed lines which will be placed around it are then marked with light pencil lines.

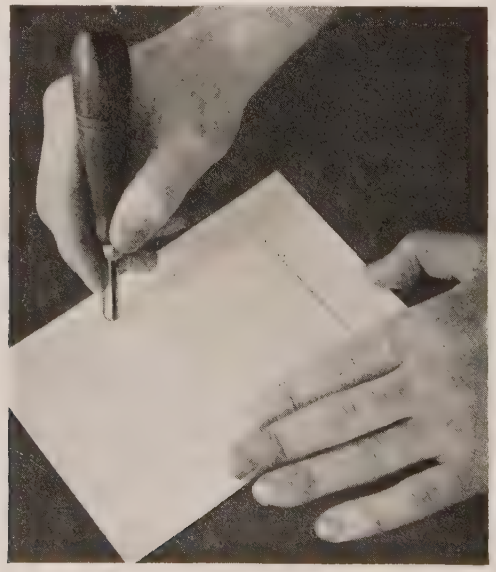

Fig. 351. Using an Embossing Tool to Prepare an Embossed Mount.

A piece of cardboard the size of the area to be depressed is cut and attached to the mount with a drop of glue placed near the center of the area to be occupied by the picture. The mount is then turned over and the back moistened with a wet sponge along the lines to be embossed. Several minutes are allowed for the water to soak in and the edges of the card underneath are located with the fingers. The mount is now embossed, or depressed, along the lines of the card underneath by following the outline with an embossing tool (Fig. 351); care should be taken to make a clean cut and uniform impression.

When this has been completed, the cardboard is torn off and the print mounted, using either a thin line of glue along the top or by dry mounting. Finally, the pencil lines are erased and the outside edge trimmed to the proper size.

Double Mounting.—First trim the print to the proper size and attach to the first mounting stock, preferably by dry mounting, otherwise by means of a thin line of glue placed on the back of the print along the upper edge.

Next, trim the mount so as to leave the desired margins around the print. The width of the margins depends upon the size and character of the print and personal preference, but should be greater at the bottom than along the three remaining sides.

Cut the card stock for the second mount a trifle large and indicate on it by light pencil lines the position of the mounted print.

Finally, attach the mounted print and trim the outside of the mount to the required size.

Commercial Mountings.—Mounts and folders (for portrait work) are available commercially, the latter particularly in large variety.

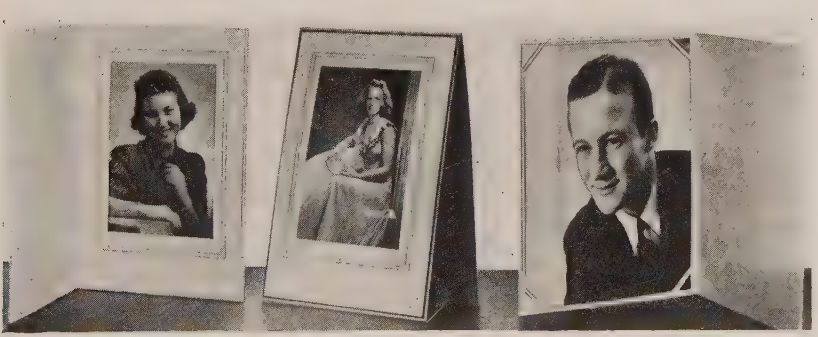

FIG. 352. Commercial Mountings for Professional Studio Portraits.

Unfortunately the artistic taste displayed in their design is frequently open to question and one is largely restricted to set sizes and proportions which may or may not be suitable for a particular print.

Folders designed for professional portraiture may be broadly divided into three classes: (1) *the inslip folder,* having an opening behind which the print is mounted; (2) *the easel folder* and (3) *the corner pocket folder,* having small pockets at each corner into which the corners of the print are inserted.

Mounting with Paste.—Prints to be mounted with paste should be trimmed first and then soaked in water for 10 to 15 minutes. Upon removal from the water, they should be placed face down on a piece of heavy glass, or a ferrotype plate, and the surplus water removed by rolling with a print roller. Photo mounting paste is applied smoothly to the backs, using a broad, flexible brush. The print is then lifted up by inserting the finger nail or the tip of a knife under one corner and placed in position on the mount. Place a clean blotter over the print and go back and forth over it until the print adheres firmly to the mount. Lack of contact can be seen by holdng the mounted print at an angle. Any raised places indicate insufficient pressure, a lump of paste, or an obstruction of some kind. If the latter, peel up one corner of the print, remove the obstacle, and go over the print with the roller a second time.

Finally, go over the surface of the print and along the edges with a moistened sponge, tuft of cotton, or cloth, to remove any paste which may have found its way to the surface of the print. Then place the mounted print on one side to dry.

Ferrotyped prints cannot be mounted with paste as the glazed surface is affected when the print is placed in water.

Dry Mounting.—Dry mounting is undoubtedly the most satisfactory of all methods of mounting. It is simple and convenient; the print is separated from any impurities in the mounting stock which might affect its permanency; and prints may be mounted on the thinnest of card without curling. It is the only really satisfactory method of mounting ferrotyped or colored prints solidly. Dry mounting tissue, which is a thin tissue coated with a composition which melts when heated, can be obtained in rolls or in cut sheets from dealers in photographic supplies and is inexpensive.

The print is first laid upon its face and a piece of dry mounting tissue of the same size attached to the back with the tip of a hot iron or an electric tacking iron. The tacking iron should not be too hot or the print may be discolored. The print is then trimmed *so that the tissue is trimmed with the print.* The print is then placed in the desired position on the mount, covered with a piece of thin cardboard and placed underneath a heated dry mounting press (Fig. 353) or a hot iron. From 15 to 30 seconds are required at a temperature of 185° to 225° F. to melt the tissue. Several impressions will be required when mounting large prints with an electric iron in order to cover the surface. The weight of the iron is usually sufficient, but do not rub.

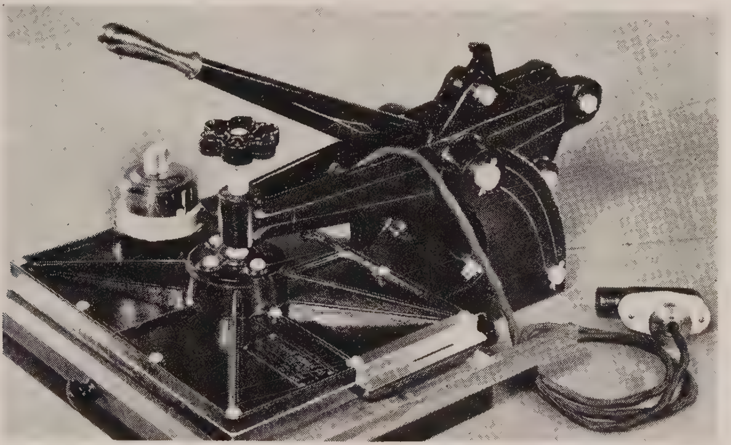

FIG. 353. Dry Mounting Press (Eastman).

If the print fails to adhere, leaving the tissue on the mount, the mounting press, or the iron, is too hot. If the print adheres to the tissue but not to the mount, the press is too cold. A temperature from 180° to 225° F. is satisfactory for most papers. Imperfect adherence of the print is usually due to uneven pressure. Irregular glossy markings or discoloration on the print are due to the press being too hot or the print being damp.

Backing Prints with Cloth.—Prints which receive considerable handling, as in salesmen's albums or in record books, are frequently mounted on cloth for added protection. Formerly, ordinary cloth was used for this purpose, but today, a special photographic mounting cloth similar to that used by bookbinders is generally employed. This stout cloth is coated on one side with an adhesive and is supplied in various weights and colors.

In mounting glossy prints, the wet print is first placed on the squeegee tin. A sheet of mounting cloth slightly larger than the print is then dipped in water momentarily, drained, and then laid over the print. Finally, the plate and its adhering print and cloth are squeegeed either with a print roller or wringer.

In mounting matt prints, the wet print is first placed on a sheet of heavy plate glass. The sheet of mounting cloth is then dipped in water momentarily, drained and then laid on the print. Finally, the print is squeegeed to the glass, then stripped and dried as usual.

Two matte prints may be mounted back to back by using the double photo mounting cloth having adhesive on both sides. One of the wet prints is placed face down on a sheet of heavy glass. The glass is placed on an illuminator or a printing machine, and the wet cloth laid down over the print. The second print is then placed in position, using the light from below to register the two prints. The prints and cloth are then stripped from the glass, squeegeed, and dried in the usual way.

Spotting.—After mounting, spots, either light or dark, should receive attention. Dark spots are usually the result of dust on the film at the time of the exposure and should be removed in the negative. If this has not been done, the etching knife must be used to scrape off the silver deposit from the spot until it maches its surroundings. If this is not done carefully, the spot may be made too light and it will be necessary to darken it with the spotting brush.

White spots are usually due to dust on the paper or negative when making the print. A little attention to the avoidance of dust at this stage will save hours in spotting the prints.

Colors for spotting photographs are supplied on celluloid cards containing four colors, black, white, cold brown and warm brown, but ordinary water colors may be used. A small sable brush (No. 1) is required. Moisten the brush between the lips and take up some of the color on the tip. Hold the brush vertically with respect to the surface of the print and bring the tip down on the print so that it covers the spot. If the amount of color deposited is insufficient and the spot is too light, take up more color and apply a second time. Should the spot be too dark, moisten another brush between the lips and remove some of the color until the spot matches its surroundings.

Large spots must be stippled in, using much the same touch as in retouching portrait negatives. If filled in solid, they are made more conspicuous.

Waxing Prints.—Prints on matt papers are frequently improved by waxing. The shadows gain in depth and appear more lustrous. Commercial preparations are available for this purpose, or a solution of paraffin wax in gasoline may be used. This is applied with a soft cloth. A weak solution of gum arabic applied with an atomizer is also very effective.

Waterproofing Prints.—Prints which are to be displayed in the open without the protection of glass or are to receive much handling should be waterproofed. Commercial preparations (Kodak W. P.) are available for this purpose, or the print may be immersed in the following solution:

Borax	30 gm.	300 gr.
Glycerin	30 cc.	300 min.
Shellac	70 gm.	600 gr.
Water	1000 cc.	20 oz.

Boil for one-half hour and add:

Methyl alcohol	250 cc.	5 oz.

Varnishing Prints.—The following formula is suitable and results in a high gloss:[4]

Transparent celluloid	1 oz.
Castor oil	⅛ oz.
Amyl acetate	16 oz.
Methyl alcohol	4 oz.

The transparent celluloid may be obtained from cleaned off film.

The dry prints are immersed in the solution for one minute, then drained, and hung up by one corner to dry.

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[4] Moir, *Brit. J. Phot.* **75** (1928) 343.

CHAPTER XXVIII

LANTERN SLIDES AND TRANSPARENCIES

Sensitive Materials for Lantern Slides.—Lantern slide *plates* are available in three degrees of contrast—soft, medium contrast, and extra contrast—and in 3 sizes, namely 2 × 2, 3¼ × 4 and 3¼ × 3¼ inches. The first two are standard sizes in this country, while the last is the English standard.

Positive motion picture film (35 mm.) on a safety base is suitable for lantern slides 24 × 36 mm. which are enclosed in 2 × 2 glass plates for use in the projector. Positive film is generally obtainable with a "regular" and a "high contrast" emulsion.[1]

The sensitometric characteristics of two typical emulsions for lantern slide materials are shown in Fig. 354. It will be observed that, as in the case of negative materials, the contrast of the image varies with the degree of development, thus providing a control over image contrast which is largely absent in positive processes on paper.

Exposing.—The maximum image dimensions on 2 × 2 slides, with most projectors, is about 40 × 40 mm. The standard mask sizes are 23 × 33.4 mm. (29/32 × 15/16 inches) and 26.2 × 38 mm. ($1\frac{1}{32}$ × 1½ inches). With 3¼ × 4¼ slides, the maximum picture dimensions are about 2½ inches vertically and 3 inches horizontally. Obviously, if the negative, or the portion of it to be included in the slide, does not exceed these dimensions, the slide may be printed by contact.

In this case, either a printing frame or a printing machine may be used. Since lantern slide plates and positive film are somewhat faster than the average contact printing paper, it may be necessary to replace the usual lamps with 10 watt bulbs, or place one or more sheets of ordinary white paper over the lamps, to obtain exposures of convenient length. The printing frame, or machine, must produce perfect contact between negative and slide plate or film. If there is any doubt on this point, a test slide should be made of a discarded negative scratched with a knife blade, and the sharpness of the image studied with a magnifier.

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[1] Lantern slides may be made directly in the camera without the necessity of making a negative through the use of reversal film now available in rolls. See p. 729.

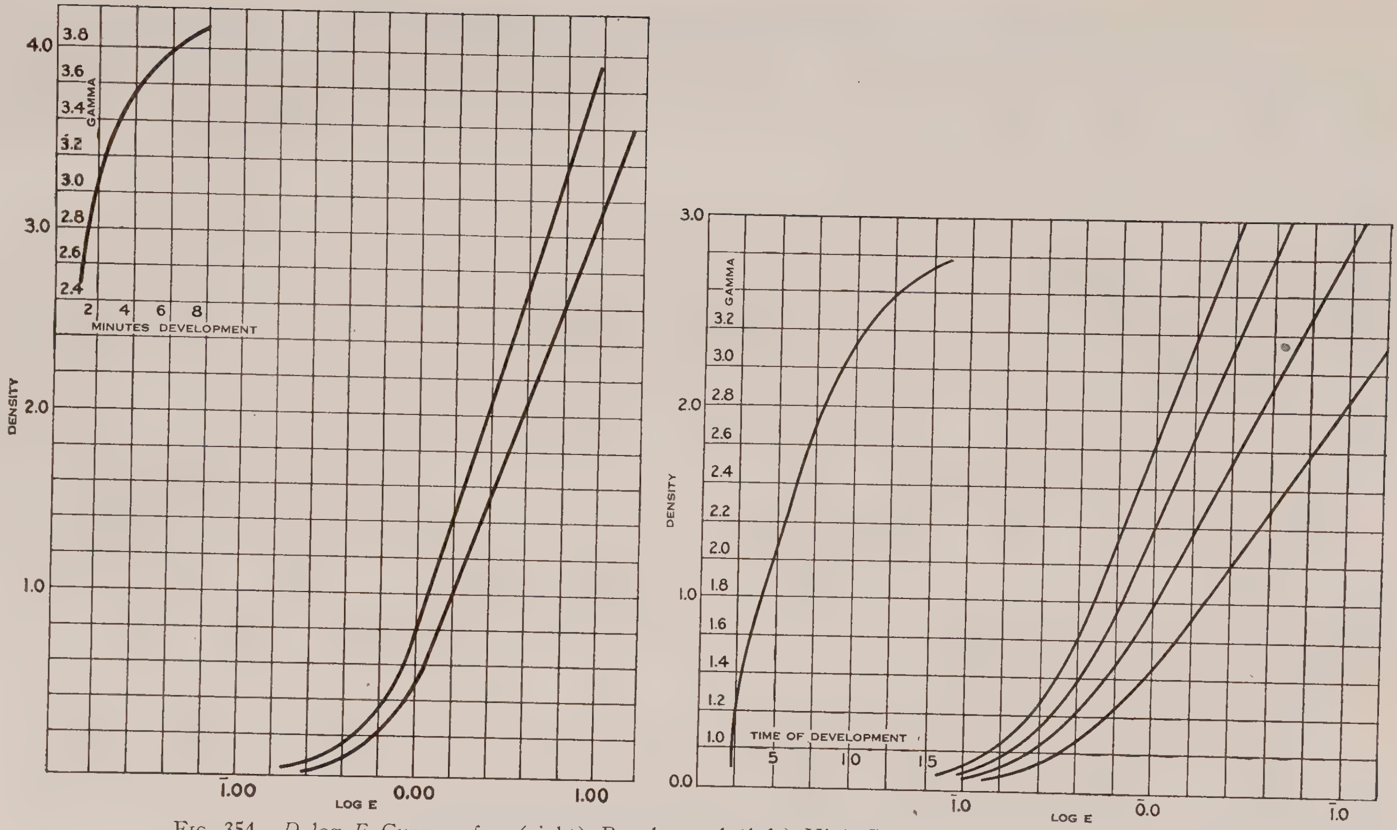

FIG. 354. *D* log *E* Curves of a (right) Regular and (left) High Contrast Lantern Slide Emulsions.

No mask of any kind should be used, as it may affect the sharpness of the image at the margins. The undesired portions of the image may be masked on the slide itself before it is bound.

Care should be taken that the vertical lines in the subject or the horizon line is parallel with the sides of the slide. It is important to remember with 3¼ × 4 lantern slides that the vertical lines of the subject must always be parallel with the *shorter* dimension of the slide.

It is well to cover the back of the slide material with a sheet of black paper or black velvet to reduce the danger of halation from light reflected back into the emulsion from the rear. Anti-halation films and plates are preferable, particularly for line work.

If motion picture positive film is used, it may be cut up into pieces about 2 inches in length or, if the negatives are of similar contrast so positive images of the proper contrast will be obtained with uniform development, the film may be exposed in strips and developed in the usual way in a developing tank.

To determine the exposure, the film or plate may be exposed in strips by placing a card over the negative and successively covering or uncovering strips of about ¼ to ½ inch wide. Upon development, the proper exposure may be determined from the exposure for the section having the required density.

If the negative is larger than the picture area available on the slide, the slide must be made by projection printing or, as it is sometimes termed, by reduction. In making reductions, the distance from the negative to the lens is greater than the distance from the lens to the film or plate, while the reverse is true of enlarging. Most projection printing equipment is suitable for making reductions, although frequently the bellows extension is insufficient. In this case, it may be possible to use a lens of shorter focal length, or to increase the bellows extension by the use of an extension cone.

An alternative method is to place an illuminator on the easel, and on this the negative, masking off all light except that transmitted by the negative, remove the lamp house and focus the image on a sheet of ground glass placed in the negative carrier of the enlarger. When sharp focus and an image of the proper size have been obtained, the ground glass is removed, the lantern slide substituted and the exposure made either by means of the shutter or, if none is available, by turning the light in the illuminator on and off.

Still another method is to place the negative on an illuminator and photograph with a camera carrying the slide plate in a plate holder fitted with kits of the proper size or a focusing camera back taking 35 mm. film in the usual cartridges. If the negatives vary in size, some arrangement for keeping the camera and illuminator in line when moving one or the other back and forth in making the different reductions will be a decided convenience.

Developers and Development.—As the sensitive materials supplied for the making of lantern slides differ in their characteristics, the formulas and developing times recommended by the manufacturer should be followed, at least until experience indicates the direction in which they may be modified for a particular purpose.

While it is quite practical to develop lantern slides by time, greater latitude is afforded by developing by inspection, as is the general practice with paper prints. Since, in most cases, as much light may be used for development as is safe for rapid projection papers, no real difficulty is experienced in following the course of development and, with a little experience, the density and contrast of the image may be judged quite accurately. With some sensitive materials, the progress of development may be judged quite accurately by the appearance of the image by reflected light, while in the developing tray, assuming of course that a white, steel enamel tray is used. When the image is examined by transmitted light, its density and contrast are seen more clearly if viewed from the support side; i.e. with the emulsion side of the film, or plate, facing the safelight. Care should be taken to avoid undue exposure to the safelight. While lantern slide materials are much less sensitive to light than negative materials, they cannot be exposed indefinitely to the light of the recommended safelights, as these have been designed to produce the greatest volume of light which is consistent with *reasonable* safety. Furthermore, fog is even more serious in a positive image for projection than in a negative. Frequent and lengthy examinations of the image during development not only increase the danger of fog from excessive exposure to the safelight, but from oxidation of the developer as well (see oxidation fog, p. 559).

Fixing, Washing and Drying.—After development, the slide should be rinsed briefly, but thoroughly, in cold water and transferred to an acid fixing and hardening bath. In warm weather, it may be advisable to harden the film or plate in a hardening stop bath of chrome alum before fixing. Fixing will require from 5 to 10 minutes in a fresh bath and should not be unduly prolonged, or the weaker densities of the image may be reduced resulting in weak "washed out" highlights.[2]

After fixing, the slide should be washed for 15 to 20 minutes in running water free of grit and sediment. A water filter may be used to advantage with many sources of tap water. Tests for the presence of hypo may be made using one of the methods described in Chapter XI.

Upon removal from the washing tray, or tank, the surfaces of the slide should be wiped free of adhering dirt and precipitated substances, using wet absorbent cotton, a viscose sponge or chamois, and then placed in a current of warm dust-free air for drying. Usually it is undesirable to force the rate of drying by the application of heat. The effect of forced drying conditions on the density and contrast of the image in general, are more marked with fine-grain, thinly coated materials of this type than with negative materials.[3]

Exposure and Development in Relation to Image Quality.—The test of a lantern slide is the image on the projection screen. If the projected image is neither too light nor too dark and has the proper contrast both for the picture as a whole and for individual tone differences to represent properly the subject, then the slide is a good one insofar as the reproduction of tone is concerned. The density-level and contrast of the slide must, therefore, be such as to produce a satisfactory *screen image* with the projector, screen, distance, etc., in use. Thus, while some idea of the quality of a slide may be obtained from direct examination in front of an illuminator, it should be projected and the screen image studied before making a final decision on its quality. The making of good slides thus involves the adjustment of exposure and development to one another so as to produce a positive image which has the proper density level and contrast to result in a satisfactory reproduction of the subject, when the slide is projected.

With a given time of development, the exposure determines the average density; the greater the exposure the higher the density level. With insufficient exposure, the density differences in the highlights are too slight to produce good reproduction of the corresponding brightness differences of the subject. The middle tones and shadows may also be lacking in density. The image as a whole, therefore, is deficient in contrast and, owing to the low density level, the projected image is too light to represent properly the subject.

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[2] Crabtree and Russell, *J. Soc. Mot. Pict. Eng.* **18** (1932) 371.

[3] White, *J. Soc. Mot. Pict. Eng.* **29** (1932) 340.

With increased exposure, the average density of the image increases and the projected image becomes darker and darker. Detail in the shadows first appears degraded and lacking in brilliancy and with still greater exposure disappears altogether. At the same time, the highlights become too dense, causing a loss in the brilliancy of detail within this portion of the image. Overexposure, therefore, results in (1) a dark screen image, (2) in lower image contrast, and (3) in degradation of both highlight and shadow detail.

The time of development affects both contrast and density. As the time of development is increased, the density range—contrast—of the image and also its average density are increased. It is obvious, therefore, that exposure and development must be properly adjusted to one another if a satisfactory image is to be obtained on the screen.

The following table may be of some value in determining the changes in exposure and development necessary to improve an unsatisfactory result.

Appearance of Slide	*Cause*	*Remedy*
Lacks density generally	Underexposure	———
Density sufficient but lacking in contrast	Underdevelopment	———
Lacks density and contrast	Underdevelopment and possibly underexposure	Develop longer, if density is still lacking increase exposure.
Too dense	Overexposure	Reduce, or better, make new slide.
Highlights weak and washed out—shadow densities satisfactory	Underexposure and overdevelopment	Increase exposure and develop for a shorter time.
Shadow densities also light and lacking in clearly defined detail.	Underexposure	———
Shadow densities lack detail—dark, highlights clouded.	Overexposure	
Shadow densities lack detail—dark, highlights satisfactory.	Overdevelopment	Reduce developing time.
Highlights clouded, shadows still lacking in density.	Overexposure and underdevelopment	New slide—less exposure and longer development. May require slide film or plate of greater contrast.

Warm Tones by Development.—Brown and brown-black tones may be obtained on lantern plates with emulsions of silver bromide or silver chlorobromide by using developers containing a silver solvent such as ammonium carbonate or thiocarbamide. The effect of using such a developer is to produce an image consisting partly of relatively coarse particles of silver and partly of finely divided particles of silver which are deposited from the developer upon the development centers, or nuclei, existing in the exposed grains. The action of the developer is thus analogous to that of the so-called "physical" developers containing free silver, the silver in this case arising from the action of the silver solvent on the emulsion in the early stages of development.

The developers used for warm tones thus form a class intermediate in character between physical developers with added silver and typical chemical developers as used for negative development.

The variations in the color of the image produced with developers of this type are due to differences in the average size (or dispersity) of the silver grains which collectively make up the deposit. The relatively coarse grains comprising the image in the case of development with the usual developers result in a deposit which is practically free from selective absorption (except in the case of developers producing a pronounced stain image). A reduction in the average size of the silver particles results in deposits possessing selective absorption, producing, as the average size of the silver grains diminishes, images having a sepia, brown, purple, red or yellow color.

Emulsions of silver chloride are not, in general, suitable for the production of warm tones by development as they develop too rapidly and tend to fog in developers containing a silver solvent.

Warm Tone Development.—The formula which follows is due to Dr. B. T. J. Glover.[4]

Metol Hydroquinone Solution A

Hot water (120° F.)	500	cc.	16 oz.
Metol	5.0	gm.	70 gr.
Sodium sulfite (des.)	25.0	gm.	350 gr.
Hydroquinone	2.5	gm.	35 gr.
Sodium carbonate (des.)	18.0	gm.	250 gr.
Potassium bromide	0.5	gm.	7 gr.
Cold water to	1000	cc.	32 oz.

Solution B

Cold water	160	cc.	8 oz.
Ammonium carbonate	20	gm.	1 oz.
Ammonium bromide	20	gm.	1 oz.
Water to make	200	cc.	10 oz.

[4] *American Annual of Photography* **46** (1930) 9.

In the table which follows are shown (1) the relative exposure times, (2) the composition of the developer, (3) the Watkins factor, and (4) the approximate color of the image.

Relative Exposure	*Developer*		*Watkins Factor*	*Color of Slide*
	Solution A	Solution B		
5	8 dr.	——	10	Olive black
10	7 dr.	1 dr.	5	Sepia
20	6.5 dr.	1.5 dr.	5	Sepia-brown
32	6 dr.	2 dr.	5	Brown
96	5 dr.	3 dr.	5	Purple-brown
300	4 dr.	4 dr.	5	Red

The exact color varies with different slide plates.

As in the case of black and white slides, density is governed by the exposure, and contrast by the time of development. However, in the case of a developer containing a silver solvent, the color as well as the contrast of the image changes with the degree of development. Beginning with a yellowish image, the color changes first to red and then to purple, brown, sepia and finally black as development progresses. Thus, with a given developer the contrast and color of the image are interdependent and neither can be modified without alteration of the other.

It is possible, however, by increasing or decreasing the concentration of the silver solvent present in the developing solution, to control the time of development necessary for a given color. This enables the contrast of the image to be altered without producing a corresponding change in color. Thus, to counteract the effect of shorter development on the color of the image, the proportion of the B solution should be reduced, while to secure the same color with increased development, the proportion of B should be increased.

The time of exposure varies with the color. While color depends upon the time of development and is independent of the exposure, it is

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Baker and Davidson—Studies in the Effect of Exposure and Development on the Color and Contrast of Warm Tone Slides. Brit. J. Phot. **71** (1924) 77.

Glover—Thiocarbamide and Blue Toned Lantern Slides. Brit. J. Phot. **70** (1923) 135.

Johnson—The Technics of Lantern Slide Making. Brit. J. Phot. **70** (1923) 237; Phot. J. **63** (1923) 58.

necessary to adjust the exposure to the time of development so as to obtain an image of the proper density. The shorter the time of development (i.e. the lower the development factor) the longer the exposure. The exposure required under any particular set of conditions must be determined by means of test exposures.

The color of the image cannot be determined precisely from the appearance of the slide during development because of (1) the color of the light transmitted by the safelight, and (2) the difference in the appearance of the image when wet and after drying. Usually the color is colder and the density greater when dry than when wet. If the time of development required for a particular color has been determined, this time should be adhered to and the density of the slide regulated by the exposure. Variation in the composition and the temperature of the developer alters color and gradation; it is well to use a small volume of fresh solution for each plate and to use a water bath to maintain the proper temperature.

Toning of Lantern Slides and Transparencies.—Lantern slides and transparencies may be toned by any of the usual processes except those involving the use of hot solutions, hypo-alum for example, or those causing softening of the gelatin. With some toning processes, however, the colors are rather too opaque for the best results. Uranium, iron and copper result in satisfactory tones in most cases as does the indirect process of sulfur toning. A wider range of colors is obtainable by dye toning. See Chapter 24 for instructions on toning.

Pleasing effects are obtainable with many subjects by tinting, i.e., uniform staining of the gelatin with a dye or a mixture of dyes producing the desired color. Whether a slide is toned or tinted, the effectiveness of the color should be determined by the appearance of the image on the screen. The appearance of the slide when held in the hand and examined by ordinary light is very deceptive inasmuch as a color which appears altogether pleasing under such conditions may be unsatisfactory when projected.

Coloring of Lantern Slides.—Lantern slides may be colored with either water or oil colors but the first mentioned are by far the more satisfactory. In general, coloring is restricted to slides in the larger size as the detail is too small for good work in the smaller size.

Slides for coloring should have a lower density, particularly in the shadows than would be suitable for the black and white slide. Slides which have been fixed in an acid fixing and hardening bath should first be placed in a 2% solution of ammonia for two or three minutes and then rinsed in plain water, otherwise the gelatin may be sufficiently hardened to repell the color.

For coloring, the slide should be supported in a slightly inclined position on a sheet of glass illuminated from below. The emulsion of the slide should be moist but free from surface water or water drops. Water colors set almost immediately so that the blending of color can be accomplished only by (1) keeping the slide moist, (2) using dilute colors, and (3) working with rapid strokes. Apply weak colors and build up to the deeper by successive applications of the color. Care must be taken to keep the color within the confines of the area to be colored. If the surface of the emulsion is wet, the color will be likely to spread into adjacent areas. If an error is made in the application of the color, the colors may be removed from the slide by placing it for two or three minutes in a 5% solution of ammonia followed by a similar period of washing in running water.[5]

Intensification and Reduction of Lantern Slides.—A slide which lacks brilliancy because of slight overexposure or a trace of fog may be improved by slight reduction in a subtractive reducer. In general, however, it is best to avoid the intensification or reduction of lantern slides, particularly those with warm tones, as the color and quality are adversely affected. If it is the exposure which is at fault, then the slide should be made over; if an alteration in contrast is required and this cannot be accomplished by suitable modification of the time of development, then the negative should be reduced or intensified.

Varnishing.—While not absolutely necessary, it is well to varnish the slide. Varnishing prevents the "dewing" of the slide in the lantern from the condensation of moisture on the cover glass when heated. Suitable varnishes may be obtained from dealers in photographic supplies. The slide should be heated to drive off all the moisture before varnishing. With some varnishes, the slide must be coated while still warm; others may be applied cold.

Masking.—Black paper masks in various sizes may be purchased from dealers in photographic supplies. These, however, are seldom the exact size required for the best composition. Masks to fit the subject may be made by means of ruled adjustable mats, with lantern slide binding strips, or a suitable mask cut from black paper.

Before binding, the slide should be marked to indicate to the lanternist the way in which it is to be placed in the lantern. Small disks of gummed paper are usually employed for this purpose. In the United States and Canada, the standard practice is to place the spot in the lower left hand corner when the slide is held as it should appear on the screen. The lanternist places the slide in the lantern upside down with the spot acting as a thumb mark. In England, the standard practice is to place two spots at opposite corners of the top of the slide, while in Europe, a single spot placed in the lower right hand corner is used.

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[5] Tobias, The Art of Coloring Photographic Prints. American Photographic Pub. Co. (Boston).

Binding Lantern Slides.—If the lantern slide is on film, it is usually placed between two pieces of glass for protection but if the slide has been made on a glass plate only a single protecting or "cover" glass is necessary and this is placed over the emulsion side. In either case the two glass plates are bound along the edges with adhesive tape (i.e. Kodatape or Scotch tape). The tape may be applied separately to each of the four sides, the strips being overlapped at the corners, or in one continuous strip. In binding by the latter method a strip of adhesive tape equal in length to the four sides of the slide is placed with the adhesive side up on a blotter or sheet of paper. The edge of the two glass plates is then placed at one end of the strip, care being taken to get it in the center so that when the tape is folded it will be the same on both sides, and the slide rotated so that it picks up the tape in succession on all four sides. The tape is then creased along the edges of the glass by pressure with the fingers and folded over on the sides. The corners may be folded over and left or clipped with the scissors so as to enable the ends to overlap.

Transparencies.—For transparencies larger than lantern slides, ordinary slow plates or film may be used, but the degree of contrast obtainable on such materials is frequently insufficient unless contrast-type developers are employed. Transparency plates and positive films coated with emulsions similar to those employed for lantern slides are obtainable from many manufacturers of sensitive materials.

In recent years, films (Adlux, Translite, etc.) and papers (Translite, etc.) coated on both sides with emulsions similar to those employed on contact printing papers have been introduced for transparencies.[6] The object of the double coating is to increase the thickness of the emulsion so as to obtain the range of densities required in a transparency. In the case of paper, the emulsions are of different speeds, that on the back of the paper being faster to allow for the loss of light in passing through the first emulsion and the paper base.

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[6] Duolux, *Phot.Tech.* I (1939) Nov. p. 50.

Duplication of Negatives.—Duplicate negatives are useful (1) as a means of preserving valuable negatives, (2) to protect the original negative from possible damage when a large number of prints must be made, (3) to enable handwork to be carried out on the duplicate negative which might endanger the original, and (4) to provide the enlarged negatives required when prints larger than the original negative are to be made by carbon, gumbichromate, platinotype or other printing processes not adapted to projection printing.

Duplicate negatives may be made by one of three methods:

1. By using direct copy film which results in a negative image directly. Sensitive materials of this type are a recent introduction, but appear to offer distinct possibilities. See p. 498.
2. By first making a positive on a suitable film or plate and from this a duplicate negative. This is the usual method.
3. By using reversing materials and reversing the positive image to a negative in processing.

Sensitive materials which produce a positive transparency direct by reversal processing have long been in widespread use for amateur cinematography and similar materials are now available for still photography. These materials are useful in making lantern slides and transparencies directly in the camera, reproducing radiographs, for photomicrography and other technical work in which a direct positive transparency is required. These films, however, are not designed for copies of line subjects. Materials of this type, processed by reversal, produce images with an extremely fine grain. In processing, the negative image is first developed, then bleached, cleared and the positive image developed. This is fixed, washed and dried as usual. The contrast of the image is fixed by the processing conditions.

Sensitive Materials for Making Duplicate Negatives.—A good duplicate negative should reproduce accurately the gradations of the original unless the contrast is to be altered in the interests of better printing quality. The definition and graininess of the image should not be markedly inferior to that of the original.

The sensitive materials used in making the intermediate, or master, positive and the duplicate negative must be able to reproduce fine detail, be free from excessive graininess, and have sufficient latitude to reproduce correctly the full range of densities in the original. These requirements are most nearly met by the special duplicating films designed for the motion picture industry. These, however, are available only as standard motion picture film.[7] Lacking these, a slow, fine-grain, blue sensitive plate or film of the "commercial" type should be used. These are preferably backed to reduce halation. Plates and films intended for transparencies, in general, are unsuitable, except for originals of below normal contrast, as the exposure scale is too limited to result in satisfactory reproduction.

Exposure and Development of the Intermediate Positive and Duplicate Negative.—Faithful reproduction of the original involves (1) the exclusive use of the straight-line portion of the characteristic curves of the sensitive materials employed in making the intermediate positive and the duplicate negative and (2) development of the two to gammas which will result in a reproduction gamma of unity (p. 447). If the contrast of the original is to be altered, then the gammas should be adjusted so as to produce the desired reproduction gamma.

The appearance of a properly exposed intermediate positive is quite different from that of a transparency or lantern slide. Since for good reproduction it is necessary that the various densities of the positive image lie within the straight-line portion of the D log E curve of the film or plate used, it is evident that the highlights of the intermediate positive will not be clear but will have a distinct density and that the whole image will be denser and softer than a good lantern slide. In fact, to the inexperienced a good intermediate positive appears overexposed and underdeveloped.

If sensitometric equipment is available, the minimum highlight density for correct reproduction with the sensitive material used is readily obtained from sensitometric strips developed under the same conditions and to the same gamma.

Lacking sensitometric data the result must be judged by visual inspection, the judgment as to quality being based upon the fidelity with which the gradations of the original are preserved rather than in the density of the image.

Fine grain developers are recommended for development and the time of development should be adjusted to reproduce the contrast of the original or, if a modification is desirable, the contrast required for good printing quality. Within the limits imposed by the plate or film, the contrast of the duplicate negative may be controlled by suitable alterations in the time of development.

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[7] For types and characteristics see: *Motion Picture Laboratory Practice,* Eastman Kodak Co., 1936.

As with the intermediate positive, sufficient exposure must be given in making the duplicate negative so that every gradation of the intermediate positive will be faithfully reproduced. Good duplicate negatives have no clear shadows, even when they are present in the original negative. The shadow portions of a duplicate negative, if properly made, are always somewhat gray, and while those in some scenes may be more dense than others, depending upon the range of brightness in the subject, none of them should be entirely clear.

Enlarged Negatives.—In making an enlarged negative there are two courses open: (1) an enlarged positive may be made from the original negative and the duplicate negative by contact printing from the intermediate positive or (2) a contact positive may be made and this enlarged to the required size. The first method involves a greater outlay for material but has the advantage that any local alterations which are needed to remove defects or to improve the composition are more readily made on the positive than on the negative as it is easier to see the effect of such alterations on the positive than on the negative.

Paper Negatives.—For broad pictorial effects where definition is not an important factor, paper is frequently employed for the enlarged negative and at times for the intermediate positive. The use of paper appeals particularly to those who wish to control the final results by altering tones, intensifying the highlights, deepening shadows or softening objectionable lines in the composition, as such work is more readily done on the back of paper negatives than on film or glass.

Any smooth, single-weight paper of suitable contrast which will produce sufficient density when viewed by transmitted light may be employed.

Transparency papers coated on both sides show less grain and produce greater contrast than single-coated papers and are suitable for negatives which are lacking in contrast.

In using a single-coated paper, graininess may be reduced by placing the paper so that the coated side faces the easel, that is away from the lens. It is, of course, necessary to give more exposure with the paper in this position than when the emulsion side is next to the lens but the improvement as regards graininess makes it worth while. The suitability of the paper positive and negative is judged, of course, by transmitted rather than reflected light.

Considerable diffusion results when both the intermediate positive and the final negative are made on paper, and except for extremely broad effects, better results are obtained by making the enlarged intermediate positive on paper and the final duplicate negative on film. This method has the advantage of the paper negative as regards handwork on the intermediate positive and the advantages of film in printing from the duplicate negative.

The transparency of a paper negative may be increased by oiling. Little improvement is made, however, in graininess, and on the whole, little is gained by oiling. The oil must be kept from the face of the print and even with the greatest of precaution, in handling the oiled negative, oil spots are liable to get on the printing paper. Oiling also increases the liability of the negative to pick up dust, grit, and lint.

McMaster—Print Control by the Paper Negative Method. Phot. J. **80** (1940) 124.

Ward—Picture Making with Paper Negatives. American Photographic Publishing Co. Boston.

CHAPTER XXIX

PRINCIPLES OF THREE-COLOR PHOTOGRAPHY

Trichromatic Theory.—All practical methods of three-color photography are based upon the theoretical investigations of Wünsch and Young (1802) into the wave theory of light and the trichromatic mechanism of color vision. Clerk Maxwell was the first to point out (1855) and demonstrate (1861) how these principles might be applied to reproduce a colored scene by means of photography. Maxwell stated that the visual appearance of any color could be matched by a proper mixture of three differently colored light sources. The three chosen colors were red, green and blue. These colors are called unitary or primary colors and their additive mixtures will match all but a few very saturated colors.

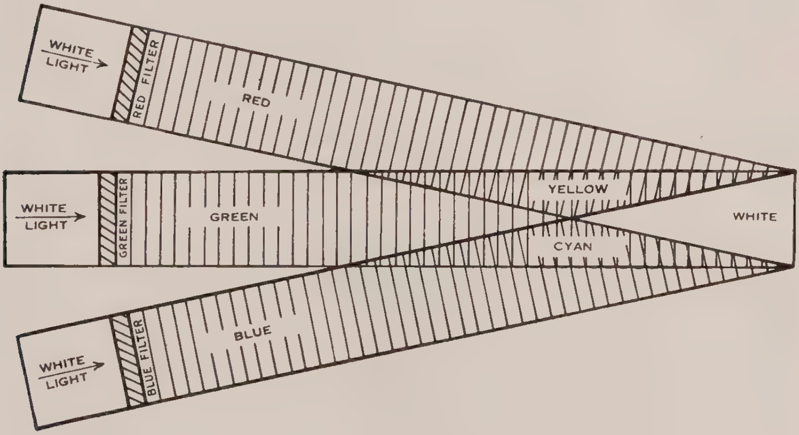

FIG. 355. Diagram of Additive Color Process Showing Mixture of Three Primary Colors Producing White Light.

If, for example, beams of white light are directed upon a screen but pass first through red, green and blue filters as shown in Fig. 355, the combination of red and green produces yellow; green and blue produce cyan; and all three together produce white. Various other colors may be produced by the combination of the primary colors in varying proportions. Thus, the addition of green to red will produce orange-red, orange or yellow, depending upon the relative intensity of the green to the red; in like manner, the combination of green and blue produces various shades of bluish-green and a combination of red and blue produces all possible shades of violet from magenta through purple.

Using monochromatic lights, the proportions of each which must be mixed in order to produce the same color sensation as is produced at any point in the spectrum itself may be determined. In Fig. 356 are shown three color-mixture curves, one for each primary color. The heights of these curves at any particular wave length indicate the proportions in which the primary colors must be combined to produce the color sensation corresponding to that wave length of the spectrum.

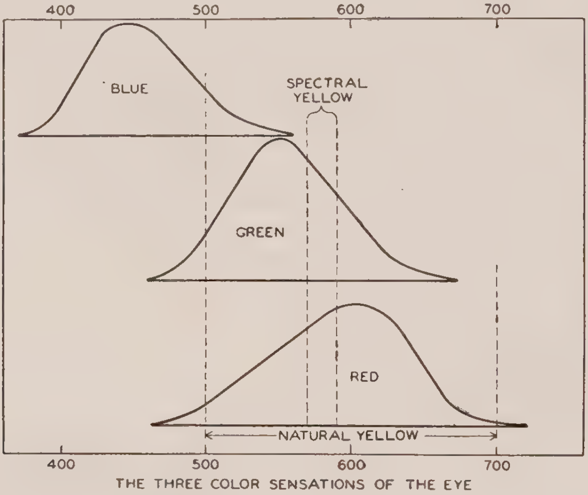

Fig. 356.

The eye is not an analytical instrument and the range of colors observed when examining a spectrum from sunlight is continuously variable—the gradual alteration of hue being due to the changing activation of the three color-sensitive elements of the eye. The eye is not able to identify the origin of colors. Thus, the visual sensation produced by a monochromatic yellow line from the spectrum, an additive mixture of limited red and green regions, and a mixture of the whole of the color range from dark red through green might be identical. Mixtures of monochromatic light of wave lengths 640, 532 and 464 mμ were found to be satisfactory for matching most natural colors.[1] It is also possible to obtain similar results with broad mutually adjacent bands of color instead of single wave lengths. The greatest range of colors can be matched, however, by using highly saturated red, green and blue colors as sources.

Maxwell's development of the theory of color photography is best expressed in his own words: "Let it be required to ascertain the colours of a landscape by means of impressions taken on a preparation equally sensitive to rays of every colour. Let a plate of red glass be placed before the camera, and an impression taken. The positive of this will be transparent wherever the red light has been abundant in the landscape, and opaque where it has been wanting. Let it now be put in a magic lantern along with the red glass, and a red picture will be thrown on the screen. Let this operation be repeated with a green and a violet glass, and, by means of three magic lanterns, let the three images be superimposed on the screen. The colour of any point on the screen will then depend on that of the corresponding point of the landscape; and, by properly adjusting the intensities of the lights, etc., a complete copy of the landscape, as far as visible colour is concerned, will be thrown on

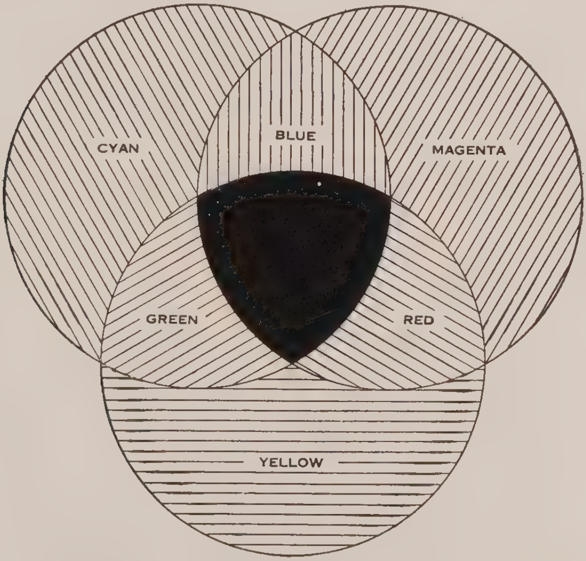

FIG. 357. Superimposed Color Filters Yield Mixture Colors by Subtraction.

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[1] Bull, *Phot. J.* **75** (1935) 257.

the screen. The only apparent difference will be that the copy will be more subdued, or less pure in tint, than the original."[2]

This method of making a colored reproduction has been called an additive synthesis, since the color was obtained by adding colored lights together on the screen to produce the various color combinations. Color may be produced by subtracting light of certain wave lengths from white light. Yellow transmits red and green and absorbs blue. Normal yellow is, in other words, minus blue; that is to say, it contains all colors of the spectrum except blue. If a yellow filter is placed on white paper and then over this a magenta filter which absorbs green light, as in Fig. 357, only red light will be reflected to the observer. Similarly, a combination of cyan and yellow filters produces green (Fig. 357) as the yellow absorbs the blue and the cyan the red, leaving only the green, and a blue image may be obtained through a combination of magenta and cyan filters.

Thus, the three "primaries," red, green and blue,[3] may be produced by subtracting color from white light. This is known as *subtractive synthesis.*

Additive and Subtractive Processes.—It has long been the custom to divide color processes into two main groups—additive and subtractive. Such a division is convenient as long as it is clearly recognized that the grouping is valid only when considering the synthesis of the color picture. The method of analysis is the same no matter which type of reproduction is to be employed. It can further be shown that optically the ideal subtractive printing colors are equivalent to the red, green and blue used in an additive synthesis. A more logical exposition is possible, therefore, if color processes are studied in the light of an additive analysis and synthesis.

If a photograph is made using a red filter, the negative will record, in terms of density, the amount of red light reflected from the subject; in other words, the greater the amount of red reflected from any particular part of the subject, the greater the density of the corresponding parts of the black and white negative. Areas which do not reflect red light are completely clear, while colors reflecting only a small amount of red are of low density.

A second negative made with a green filter will record the green, and a third negative made with a blue filter will record the blue reflected from the various parts of the subject. Hues that may be formed from

[2] Maxwell, *Trans. Roy. Soc. Edinburgh* 21 (1855) 275.

[3] The blue primary is often designated by the term blue-violet.

two or more of these colors will be recorded on two or more negatives in accordance with the amount of light of each primary color reflected. Thus, the three negatives collectively will record, in terms of silver densities, all the colors of the subject.

If black and white positive transparencies are made from these negatives, color will be indicated by *lack of density.* In the positive from the red separation negative, for example, areas corresponding to red parts of the subject will be almost clear, those containing some red represented by a low density and those without red by a relatively high density.

This transparency, when illuminated with red light, will reproduce the red component of the various parts of the subject. In like manner, transparencies from the other negatives will reproduce the corresponding color components of the subject when illuminated by light of the same color as used in making the negatives.

It is now only necessary to superimpose the three colored images to produce a representation in full color of the subject photographed. This may be done in one of two ways: (1) the three positives may be placed in a specially designed triple lantern which is so arranged that the three images can be made to coincide upon the screen, or (2) the three positives may be placed beneath filters and the images superimposed with the aid of mirrors in an instrument known as a *photochromoscope* (Fig. 358). A modern form of this instrument is available as the Curtis Color Analyst.

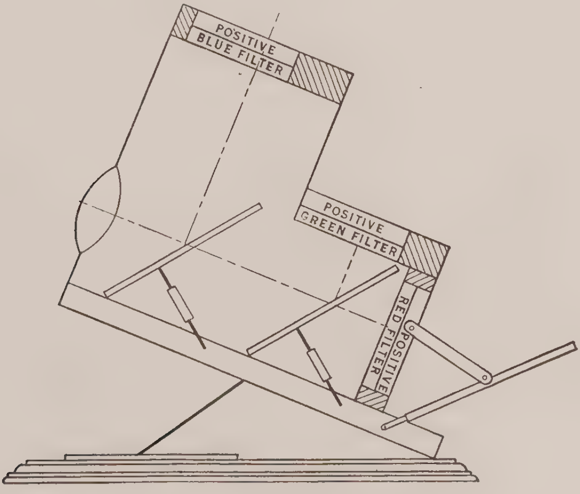

Fig. 358. Photochromoscope.

There have been many attempts to utilize this system of making colored pictures. As will be shown later, the color fidelity of such methods is quite high, but because of expensive and inconvenient viewing or projecting devices, they have never attained widespread popularity. The widest field for these methods has been in color motion pictures.

Color Screen Materials.—Screen materials, discussed further in Chapter XXXII, are now by far the most important of the additive processes of color photography. In just the same way that a painter may secure a certain color by the admixture of dabs of pigment of two or more colors which, at a suitable viewing distance, are no longer seen individually but combine to form a single color, so it is possible to secure all three color-sensation records on a single plate by exposing it behind, and in contact with, a screen composed of a large number of red, green and blue filters so small as to be indistinguishable to the unaided eye.

Screen materials may be divided into two types; in one, the small filters are arranged in a regular pattern, in the other, the differently colored filter elements are distributed at random forming an irregular mosaic screen. With screens of the first type, the screen may or may not be on the same support as the photographic emulsion. In the second type of screen, the photographic emulsion and the screen are coated onto the same support and cannot be physically separated. Whenever the screen and photographic emulsion are inseparable (irregular mosaic or some regular screens), the emulsion is developed to a negative and reversed to yield a positive color transparency. If the photographic emulsion and screen may be separated physically (some regular screens) the emulsion may be developed to a negative and a print made onto another emulsion which is then registered with a color screen to yield the positive color transparency. Separable screen materials are coated onto glass supports while the inseparable materials may be coated onto film base. In either case, the color screen lies between the light sensitive emulsion and the camera lens.

In Fig. 359, beams of red, green and yellow light are represented as falling on a screen composed of small filters designated R (red), G (green), and B (blue). Red light is transmitted by the red filter (R) and renders the emulsion beneath it developable. Green light is transmitted by the green filter and the emulsion beneath is rendered developable. Yellow light is transmitted by both the green and red filters, rendering the emulsion beneath both developable.

Klein—Colour Cinematography.

The deposits of silver produced upon development are shown by the darkened portions.

If the negative image is reversed to form a positive, or a positive is made from the negative and placed in register with the screen, red light is reproduced by the light transmitted by the red filters, since the green and blue filter elements are covered with the silver of the positive image. In the same way, yellow is reproduced by the light transmitted by the green and red filter elements, only the blue being obstructed by the positive silver image.

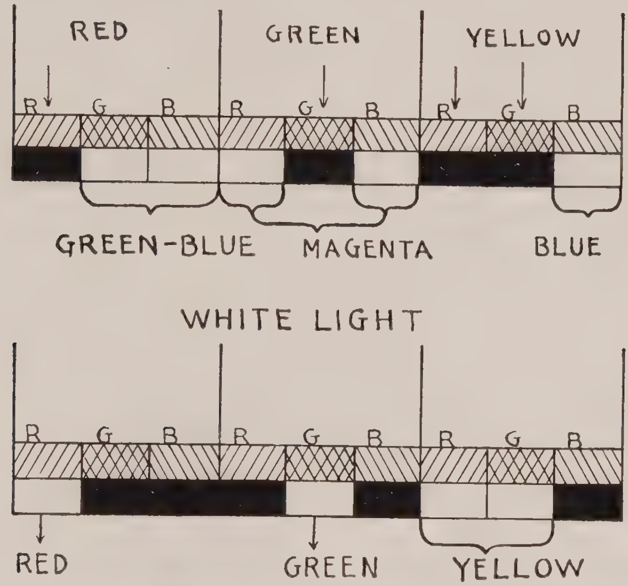

Fig. 359. Principle of Screen Plates.

If the screen material is developed to a negative, not only will the subject values be reversed but the colors will all be complementary to those of the original. A silver negative and a color negative will be obtained. The red will be represented by a mixture of green and blue, the green by a mixture of red and blue (magenta), and the blue by a mixture of red and green (yellow).

Subtractive Processes of Color Photography.—Three-color negatives may be made in the same manner as that employed for making

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The Dufaycolor Book.
Practical Color Photography with Finlay Natural Color Process.

negatives to be used in an additive process and are similar in every respect. Negatives for subtractive printing may be made (1) by making three separate exposures with an ordinary camera, changing the sensitive material and filters between each exposure, (2) by means of a repeating back which enables these changes to be made in a much shorter period of time, (3) by using a tripack in which three emulsions, each recording one of the primary color-sensations only, are placed in contact with each other and exposed, (4) by using a tricolor camera in which all three negatives are exposed at the same time through the same lens, and (5) by making use of a screen or integral tripack transparency to record the separations and later to re-separate the color records onto three negatives. All of these methods will be described at greater length in the following chapters.

To obtain a positive in color from negatives produced by any of the above methods, it is necessary to superimpose three images of the proper colors. Since each of the negatives constitutes a record in terms of density of the distribution of one particular color in the subject, it is obvious that the densities of the positive will indicate not the presence of that particular color sensation but its absence. In other words, the densities of the print from the red filter negative will indicate not the amount of red reflected by the corresponding portions of the subject, but the absence of red, that is, the light of the other regions of the visible spectrum. Hence, the color of the positive image will not be that of the filter used in making the negative, but complementary to it. In other words, the red filter negative will be printed as a cyan (blue-green) or minus red positive; the green filter negative printed as a magenta or minus green positive; and the blue filter negative printed as a yellow or minus blue positive.

Subtractive Printing Processes.—The methods employed in making the color images for subtractive printing processes may be divided into six classes:

1. *Toning processes.*

(*a*) Positives are prepared from the three negatives and are then chemically toned to produce images of the required colors. The combined positives yield the final picture as a transparency or paper print.

(*b*) Positives are prepared from the three negatives and the silver images are converted to compounds which will absorb, or *mordant,* various dyes. After dyeing with the appropriate, usually basic, dyes, the combination of the three colored images yields the final color picture. Since the dye is distributed throughout the layer wherever the silver image was present, the final result is composed of three such layers.

2. *Relief processes.* Positive or negative gelatin reliefs are made from the three color records by means of tanning development, etching, hardening, bleaching, or the reaction of silver or light and dichromated colloids. The gelatin reliefs may be either of the following:

(*a*) Clear gelatin on a film or glass support which is dyed with suitable minus-color dyes. These dyes are then transferred by imbibition to a gelatin coated paper or film. The reliefs may be redyed for successive printings.

(*b*) Pigmented gelatin composed of insoluble pigments suspended in the gelatin. The three pigmented gelatin reliefs are superimposed to form the complete picture.

3. *Selectively hardened gelatin processes.* These processes are based upon the water or dye-absorbing properties of hardened and unhardened gelatin. They differ from the imbibition processes discussed under 2 (*a*) in that the whole of the gelatin remains, while in the processes discussed under that heading, a gelatin relief is formed through the removal of a part of the original gelatin layer.

The color records are placed in a hardening bleach which removes the silver image and hardens the gelatin in proportion to the density of the original silver image. This results in colorless images of differentially hardened gelatin. Such films may be stained with dyes having an affinity for soft or hard gelatin depending upon the type of image desired. Similar differential hardening of gelatin is also used in some of the ink transfer processes which make use of the varying water absorption of such a gelatin layer. Greasy inks are repelled by water-bearing gelatin and held by the unsaturated portions. The inks may then be transferred to a paper support.

4. *Dye coupling development processes.* The oxidation products of certain developers yield brightly colored dyes. If photographic emulsions are exposed and then developed in the proper dye coupling developers, a colored dye and a silver image are obtained. By the proper choice of processing solutions, either the subtractive printing colors cyan, magenta and yellow may be procured or almost any other colors desired. Dye coupling development may be employed to obtain three colored positive images for superimposition or may be applied to integral tripacks for the production of color transparency negatives or positives or for positive prints (see Chapter XXXIII).

5. *Chemical dye destruction processes.* Certain dyes are capable of being destroyed in the presence of silver by treatment with appropriate chemical solutions. If a layer of emulsion is dyed and then exposed and developed so that a silver image is obtained, the dye may be destroyed in proportion to the amount of silver present at any point. If the silver is removed, a dye image will remain in the emulsion layer. The process may also be worked with other dyes that are capable of destruction only in the absence of silver. Such procedures may be employed to obtain color prints either in separate emulsion layers which may be superimposed to yield a color picture or, more commonly, in connection with the integral tripack color materials (see Chapter XXXIII).

6. *Dye bleaching processes* (*light*). Many dyes are rather unstable and fade readily upon exposure to strong light. If a three component mixture of the proper subtractive color dyes is exposed under a color transparency, a color print is obtained directly due to the absorption and subsequent bleaching of the dyes as they absorb complementary colored light (see Chapter XXXIII). This is undoubtedly the most straightforward method of color printing but, because of technical difficulties, it has not been commercially successful.

Another form of dye bleaching is based on the photochemical reaction between light and a sensitive diazo compound.[4] The diazo compound is bleached in the areas exposed to light and a colored image produced by the application of a chemical developer which converts the diazo compound into a stable dye image. Since it is the unexposed diazo compound which is used in the formation of the image, it is evident that a positive is obtained from a positive; thus, it is necessary to print from positives rather than from original negatives.

Subtractive Processes Based Upon an Integral Tripack.—Ducos du Hauron, who seems to have anticipated almost every possible process of color photography, suggested the use of three emulsions each separately sensitized to one of the three primary colors, superimposed, as a means of making three color negatives. The simplest method of making such a tripack is by superimposing suitable emulsions coated on three separate films.

Tripacks in which the three emulsions are coated over one another on the same film are termed "integral tripacks." The first tripack of this type to be introduced commercially for camera use was developed in the research laboratories of the Eastman Kodak Company and introduced as Kodachrome, first for amateur cinematography and then as 35 mm. and cut-sheet film for amateur and professional use.

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[4] Spencer, *Brit. J. Phot. Col. Suppl.* **22** (1928) 30.

The trend in modern color photography is definitely toward the integral tripack type of material for both reversal, negative-positive, and printing methods. For a detailed discussion of the types of integral tripack, see Chapter XXXIII.

Kodachrome. Kodachrome films are coated for use with three different illuminants. Regular Daylight Kodachrome is balanced for an illuminant having a color temperature approximating sunlight, or 5600° K. Type A Kodachrome, available as amateur motion-picture and 35 mm. film, is balanced for an illuminant of 3450° K., while Type B Kodachrome, available in cut-sheet only, is balanced for an illuminant of 3200° K. The moderate speed of these materials enables them to be used for all photography under conditions not unlike those applied to black and white photography.

Owing to the complicated processing technique necessary, and the high degree of precision with which the various operations must be controlled, the film cannot, in its present state, be processed by the user but must be sent to the Eastman Kodak Company for development. The processed film consists of three layers of dye, obtained by dye coupling development, together composing the finished color transparency.

Kotavachrome and Minicolor. The Kodachrome dye coupling process is applied in a slightly revised form to yield Kotavachrome and Minicolor prints. The construction and color formation are similar except for the different contrasts required for a print to be viewed by reflected light. The base supporting film is pigmented white cellulose acetate. Color transparencies may be printed directly onto these two materials either by contact or projection. Processing must again be carried out by the Eastman Kodak Company.

Agfacolor. The Agfa process ultilizes an integral tripack and is made on 16 and 35 mm. film base. The exposure and results from Agfacolor are similar to those obtained from Kodachrome, the difference between the two processes being in the method of formation of the dye images which comprise the final transparencies. This is also a dye coupling process.

Kodacolor. This new integral tripack is developed to a color negative and printed onto a similar tripack material on a paper support to obtain a positive color print. The negative material is now available in most roll film sizes.

Gasparcolor. Gasparcolor is another integral tripack process differing from the aforementioned types in that the dyes are incorporated in the emulsions during manufacture. Gasparcolor is a dye destruction process and, at the present time, is only used for making motion picture release prints from various types of separation negatives.

Two-Color Processes.—Pleasing, although obviously incomplete, pictures in color may be obtained of certain subjects using only two (orange and cyan) primary colors. Two-color negatives can be made with one exposure, in an ordinary camera by using a bipack (see p. 749), and printing processes employing two images are naturally simpler than those employing three colors. The complications of the three-color processes have led numerous investigators to attempt to perfect two-color processes, particularly for making motion pictures in color. There is, at present, a declining interest in two-color processes and it is probably safe to say that such processes will soon be chiefly of historical interest.

In two-color processes, the spectrum is either divided into approximately equal parts by the taking filters, the orange and red being recorded on one negative, and the green and blue on the other, or one of the tricolor primaries is ignored altogether, the choice depending upon the type of subject and illumination for which the process is designed.

When the spectrum is divided into two approximately equal parts and the prints are made in color complementary to those of the taking filters, flesh values are reproduced quite well.

Yellow and purplish-blue are not included, nor white, although as du Hauron pointed out, the yellow sensation is produced if the results are viewed in a yellowish light and the degraded whites produced by two-color processes frequently appear practically white due to the contrast of the other colors. Suggestions have been made that the usual three color prints be made, the yellow image being exposed partly from the blue-green and partly from the red negative. While such methods, under certain circumstances, produce pleasing results, it is obviously impossible to reproduce more than one or two colors or their mixtures accurately in this manner.[5]

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[5] Ives, *Camera,* Phila. (1933) 33.

CHAPTER XXX

THREE-COLOR NEGATIVE MAKING

The purpose of a set of three color separation negatives is to record in terms of black silver deposits the relative amounts of the three primary colors, red, green and blue-violet, present in the subject being photographed. The three records obtained, after development, are then used as light valves to control the intensities of red, green and blue-violet light that will finally make up the reproduction—whether in the form of an additive mixture of lights on the screen or a subtractive mixture of dyes, pigments or inks.

Since the color images must be superimposed in the final result:

1. The three images should be the same size,
2. The three images should be made from the same position, and
3. The three images should be equally sharp in all portions.

Since each negative must represent in terms of density the amount of light of a particular primary reflected from the different parts of the subject:

1. The filters should divide the spectrum into three approximately equal parts with some overlapping to ensure complete coverage, and
2. The rendering of a scale of grays should be the same in all three negatives in order to obtain color-free rendering of white and grays, and to ensure the proper balancing of the color records when making the reproduction.

Filters for Three-Color Photography.—The filters used to limit the range of wave lengths recorded on each separation negative have been well standardized in practice. Suggestions put forward to the effect that the transmission ranges of the filters should correspond to the color mixture curves have been extensively debated since the turn of the century.[1] The filters giving the most satisfactory color reproductions with the practices in common usage were, however, much more abrupt in their division of the spectrum. The early ideals were of the type shown in Fig. 360. The spectrum is divided by filters of this type into three broad and two narrow bands. From 600 mμ to 700 mμ is recorded in the red filter negative only, the region between 580 mμ and 600 mμ is recorded through both the green and red filters and is reproduced as yellow, since yellow results from the admixture of red and green light. The region between 500 mμ and 580 mμ is recorded only in the negative made through the green filter, while the region between 480 mμ and 500 mμ is recorded in both the green and blue filter negatives and, therefore, is reproduced as cyan. The region between 400 mμ and 480 mμ is recorded only on the blue filter negative and is reproduced as blue. While it is not possible by using these filters to produce a distinction between hues which lie totally within any of these spectral regions, in practice this deficiency is not serious, since naturally occurring colors reflect light of nearly all visible wave lengths, their hue being due to a reflection peak in some region of the spectrum.

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[1] Bull, *Phot. J.* **75** (1935) 257. Spencer, *Phot. J.* **75** (1935) 337. Murray and Spencer, *Phot. J.* **78** (1938) 474.

GEOGHEGAN AND SMETHURST—Brit. J. Phot. **85** (1938) 339.

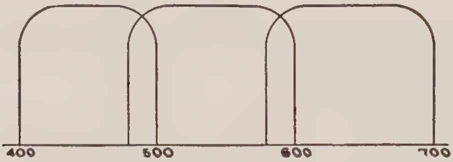

Fig. 360. Curves of the Ideal Three Color Filters (Photography of Colored Objects).

These "ideal" filters would not, of course, enable one to distinguish between two blues, for example, at 430 mμ and 450 mμ, both being recorded only on the blue record negative. A photograph of the spectrum, therefore, would only record as a five-colored band of light, there being no separation of hues within the five divisions. Fortunately, the subjects generally photographed do not reflect monochromatic light, the distribution of light from all common objects being selective through the spectrum to give the object its color but there is usually some reflection at all wave lengths (Fig. 361). The dyes and coloring materials available for the manufacture of color filters necessitated some departures from the generally accepted (see Chapter XXXIV) ideal transmission curves. Spectrophotometric curves showing the transmission of a well-known set of three color filters (Wratten, No. 25 (red), No. 58 (green) and No. 47 (blue-violet)) are shown in Fig. 362. The transmission curves of the red and the blue filter approximate the ideal very closely; the transmission of the green filter

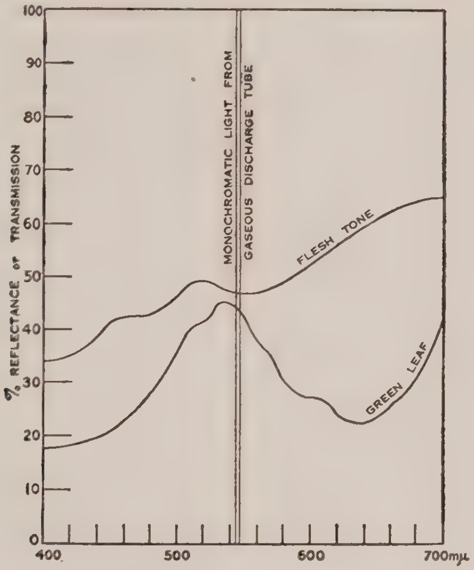

FIG. 361. Comparison Between the General Spectral Reflectance of Natural Colors and the Single Wave-Lengths from Monochromatic Light Sources.

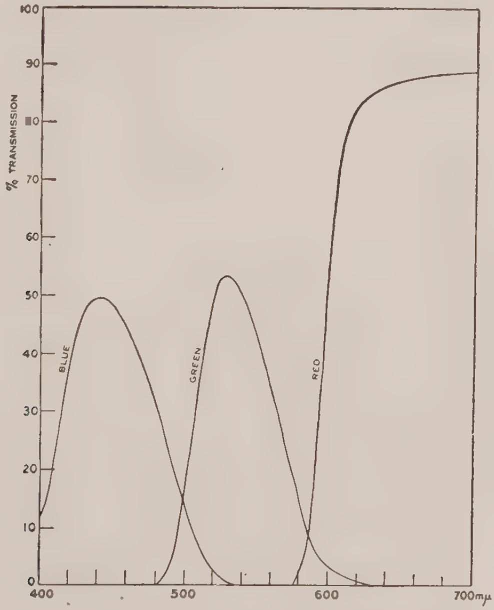

FIG. 362. Transmission Curves for a Set of Standard Tricolor Filters.

ends less abruptly at the long wave region than that of the ideal. While this can be overcome by increasing the red-absorbing component of the green filter, such a procedure is not practical because of the increase in the filter factor, necessitating greatly increased exposure.

It is possible to obtain the desired colored records by other than standard tri-color filters as indicated in the following section on negative materials. With other than the normal panchromatic emulsions, yellow, violet or other color filters may be required.

Modern tri-color filters are available as films of colored gelatin or similar material, colored gelatin cemented between glasses, colored optical glass and plastics. Liquid filters, although not common, can be used. The solid optical glass filters are probably both the most durable and the most permanent. The coloring matter in many filters is quite susceptible to light and fades upon prolonged exposure. Standard tri-color filters are fairly stable although not equally so.

Exposure of Color Separation Negatives.—Color separation negatives may be made in a variety of ways as the following table will show. In this chapter, we shall only consider the records made with a lapse of time between each exposure or instantaneous exposures of the physically separable type. Any of the following methods yield records of the primary colors present in the subject in terms of silver deposits:

I. Successive Exposures.
    A. Direct successive exposures.
    B. Repeating backs.

II. Simultaneous Exposures.
    A. Physically separable records.
        1. Bipacks and tripacks.
        2. Beam splitters.
    B. Physically inseparable records.
        1. Lateral separation—one emulsion.
            a. Screen processes.
            b. Lenticular processes.
        2. Vertical separation—integral tripacks and bipacks.
            a. Differently sensitized emulsions.
            b. Emulsion layer sensitization.
    C. Miscellaneous combinations.
        1. Screen bipack.
        2. Lenticular bipack.

Direct Successive Exposures.—For still objects an ordinary camera may be used, the three negatives being made by successive exposures, the filters and the plates or films being changed between each exposure. The exposure must be adjusted, of course, in accordance with the multiplying factors of the filters. Care must be taken that the lighting does not change during the time the three exposures are being made and that a rigid camera and tripod are used to prevent any danger of shifting position when changing plates and filters. Neither portraits nor landscapes in which movement is likely can be photographed in this way.

Repeating Backs.—An improvement over the ordinary camera with separate emulsions and holders is provided by a repeating back. The holder of the repeating back takes a plate long enough for the three exposures, or three separate small plates, and the filters are placed in front of each plate so that filter and plate are changed together for each exposure. In some cases the repeating back is shifted from one exposure to the next by hand and in other cases the holder automatically drops into position for the next exposure when the shutter closes. With repeating backs of this type, all three exposures may be made in the space of three or four seconds.

Bipacks and Tripacks.—A bipack consists of two separate emulsions held face to face in one holder, both being exposed at the same time. A red recording emulsion is generally used as the rear element of the bipack, preceded by an orthochromatic film with a red filter surface coating. This combination is not essential as other pairs may be used. A bipack may be employed as the negative material for two-color processes or it may be used with an appropriate filter as a means of recording two of three color separations for a three-color process. A typical tripack consists of three separate films. The film in front is first coated with an ordinary (blue-sensitive) emulsion and then with a layer of gelatin, containing a yellow filter dye. The second film is coated on the front side with an orthochromatic emulsion sensitive to green and on the back with a gelatin layer containing a red dye. The first and second films are exposed with their emulsions in contact. The rear film (third) is coated with a panchromatic emulsion. Thus, upon exposure in the camera, a blue-violet record is made on the front film, a green on the second and a red record on the third, or rear, film. Other emulsion combinations and orders may also be used.

Potter—Methods of Making Three-Color Separation Negatives. Defender Photo Supply Co.

There are five drawbacks to the widespread use of the tripack as a means of making three-color negatives:

1. *Unsharpness of the second and particularly the third images.* The scatter of light in the first emulsion necessarily results in a loss of definition in the second image and, since such effects are cumulative, the loss of definition is even more marked in the third image. This limits the tripack to work in which critical sharpness is not required.

2. *Limited exposure latitude.* This is due to the fact that the first and second emulsions must be as thin as possible in order that the maximum amount of light may reach the rear film, and thin emulsion layers have little latitude because any appreciable increase in exposure leads to the maximum density which the emulsion will produce. Any overexposure leads to excessive image unsharpness in the third negative.

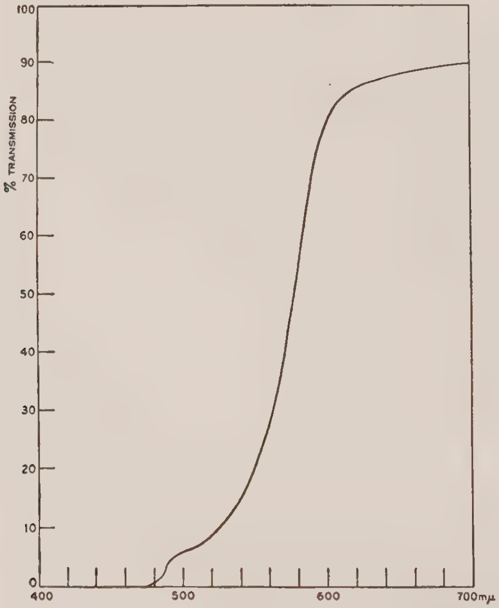

Fig. 363. Wide Transmission Band of a Typical Tripack Red Filter.

3. *Difficulty of securing balanced exposures.* This is due to the necessity of adjusting the relative speeds of the three emulsions so as to obtain equal densities on all three negatives with the same exposure. This is a difficult manufacturing problem.

4. *The comparatively long time of exposure.* Owing to the absorption of light in the first two films, a comparatively long exposure is required for the rear negative despite the fact that a highly red-sensitive panchromatic material is employed.

5. *Inferior color separation.* Because of the necessity of maintaining reasonable exposure times, the red color filter layer transmits more in the yellow and orange regions of the spectrum than is desirable (Fig. 363).

For work not requiring the delineation of fine detail or color accuracy, the modern tripack is quite satisfactory. Its special field of usefulness lies in portraiture where the diffusion of the red record is usually of no concern.

Tricolor Cameras.—Tricolor cameras are designed to divide optically the light transmitted by the lens in such a manner as to produce two or three separate images in different planes. Such devices are sometimes called beam-splitters. A great number of methods of dividing the light from the lens have been developed but the only types of interest here are those in which the whole area of the light cone transmitted by the lens affects each separation. The tricolor cameras in present usage may be divided into (1) the single mirror, and (2) the double mirror types. In the single mirror camera, two images are formed, one transmitted directly through the mirror, the other reflected from the front surface of the mirror. In this type of camera, a bipack is exposed at one negative position and a single film at the other. In the double mirror camera, one image is formed after passing through both mirrors, the other two after a reflection.

The design of the optical system in one-exposure color cameras is limited by the requirement that each emulsion must be evenly illuminated. Lack of observance of this requirement leads to what is known as "color wedging"—a variation in negative density across the emulsions but not the same on each separation. The change in ratio of reflected and transmitted light with varying angles of light incident on the mirrors makes this condition difficult to satisfy. In Fig. 364, three representative camera constructions are illustrated. In type A, the two mirrors are parallel and there is some color wedging on the second and third images. In type B, the two mirrors are at right angles to each other so that one reflected image is either above or to the left of the

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Coote—Phot. J. **81** (1941) 293.
Klein—Colour Cinematography.
Wall—History of Three-Color Photography.

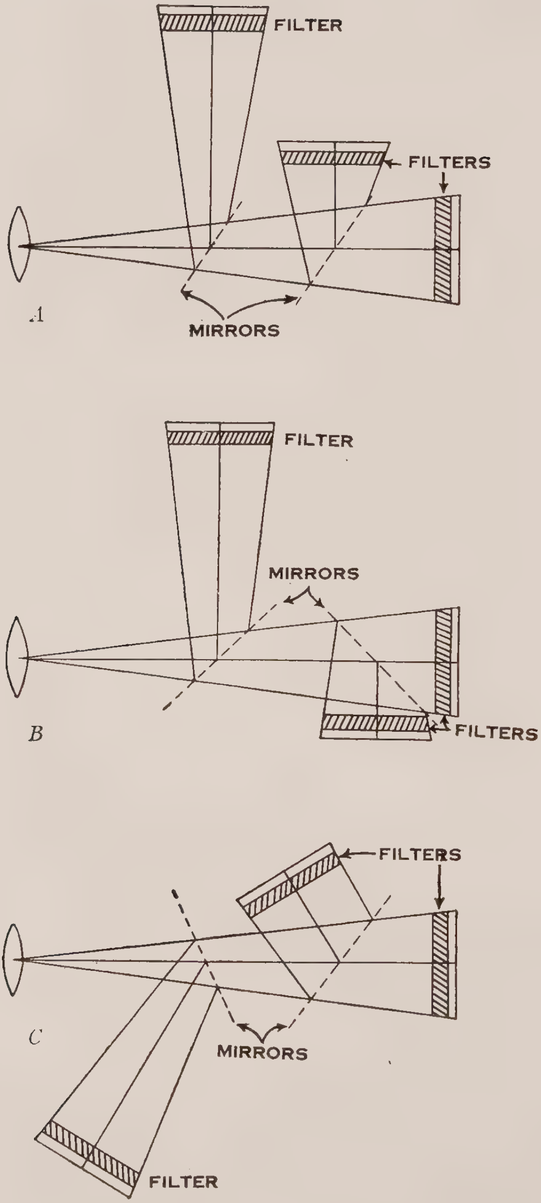

FIG. 364. Three Types of Double Mirror Color Camera Construction.

direct image, the other below or to the right. The advantage of this arrangement over some others is that the tendency towards uneven illumination of the direct and second reflected image is exactly corrected by having the mirrors at right angles. In type C, the mirrors are not at 45° to the optical axis of the lens. This type of construction yields negatives, when properly baffled inside the camera housing, that are quite free from color wedging and seems to be the most common type of present day construction.

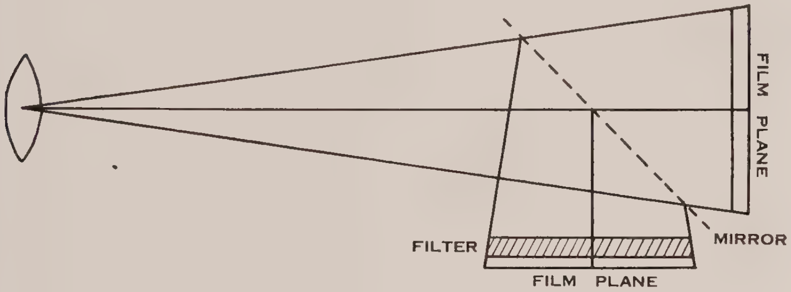

Fig. 365. Single Mirror Color Camera Using a Bipack. Mirror Angle May be Increased Over 45° to Obtain More Even Illumination.

The optical construction of the single mirror camera is shown in Fig. 365. In single mirror cameras, sometimes called "bipack and singles," there are three possible separation combinations. The single film may be either a red, green or blue record in which cases the bipacks will record blue and green, blue and red, or red and green respectively. There are many emulsion filter combinations that can be used to obtain the three types listed. In the first place, for example, the single film would be a panchromatic emulsion exposed behind a red filter, and the bipack a combination of yellow-dyed blue-sensitive film and an orthochromatic film. In the second case, the single film might be an orthochromatic emulsion behind either a yellow or green filter and a bipack of blue sensitive or orthochromatic front film with a red filter layer and a panchromatic rear film, the pair being exposed behind a magenta filter. The third possible combination consists of a single blue sensitive emulsion without a filter or with a magenta or violet filter and a bipack of orthochromatic red-surfaced and panchromatic emulsions in contact behind a minus blue filter. The arrangement chosen depends upon the emulsion combinations available and the reflection-transmission ratio of the mirror in the camera. The performance of the single mirror camera depends upon the quality of the negatives produced by the bipack, that is, on (1) the color separation obtained, and (2) the sharpness of the image obtained on the rear negative of the bipack. On the other hand, the single mirror camera, being much simpler than the double mirror camera, is less expensive and permits shorter exposure. With the proper choice of subject the single mirror camera yields very satisfactory results.

The modern tricolor camera is generally of metal construction. The partially reflecting mirrors are made either of glass or of thin membranes of collodion stretched over an optically flat metal frame. These latter are called pellicle mirrors. Whichever form of mirror is used, it may be clear or colored and its surface may be partially metallized to obtain the desired reflection-transmission ratio. Pellicle mirrors have rapidly replaced the glass mirrors formerly found in one-shot cameras. Because of the thickness of glass mirrors, unless special precautions were taken, a double image was obtained on the reflected beam due to reflections from both the front and rear surfaces of the glass. This was sometimes overcome by making the mirror serve as a filter so that the back surface reflection would be minimized. The color of the filter was usually complementary to the separation negative filter. Such an arrangement, of course, would not allow of any alteration in position of the separation negatives for different type illuminants. A further disadvantage of glass is the refraction of the light passing through the thickness of the glass mirror. Due to this refraction, one half the image is expanded, the other half contracted. This makes registration difficult and no really satisfactory permanent compromise can be reached for the refraction distortion.

All these disadvantages are readily overcome by the use of pellicle mirrors, which are so thin that the refraction and double image errors are small enough to be negligible. These membrane mirrors may also be dyed if necessary, although this is not common practice at present except in single mirror cameras. The only drawback to the thin membrane type mirror is its susceptibility to mechanical damage. It has been proved conclusively that under normal atmospheric conditions no difficulty is experienced if reasonable care is exercised.

Sensitive Materials for Three-Color Photography.—For three-color separation work, the only requirement is that three negatives finally be obtained which are records of the red, green and blue in the subject. The following combinations may be used:

Red Record	*Green Record*	*Blue Record*
Panchromatic Emulsion Red Filter	Panchromatic Emulsion Green Filter	Panchromatic Emulsion Blue Filter
	Orthochromatic Emulsion Green Filter	Orthochromatic Emulsion Magenta Filter
	Orthochromatic Emulsion Yellow Filter	Non-color Sensitized Emulsion without Filter or with Blue-transmitting Filter

The combination chosen depends on many factors such as availability, speed and the characteristics of the various sensitizings. In favor of using one panchromatic emulsion with the appropriate filters for all three exposures, it has been stated that the sensitometric characteristics of the three records will be the same and that, upon keeping, the relative speeds and gradations for each color record will change in a similar manner. The arguments in favor of separately sensitized emulsions revolve about the desire for speed. Because of the low light efficiency of the standard green and blue tricolor filters, a much faster combination is obtainable from a yellow filter on the green record and a violet or no filter for the blue record. Some observers find that the sensitometric characteristics can be matched about as closely with different emulsions as with a single panchromatic one.[2] The emulsion recording the red separation should be of the medium red sensitivity type. Since accurate color reproduction necessitates the use of the straight portions of the emulsion's characteristic curve and a wavelength-gamma variation as small as possible, these factors should be considered when choosing emulsions for color separation.

For three-color photography, glass plates have the advantage of being free from unequal expansion or contraction in processing which would disturb the registration of the three color images. Experience has shown, however, that films may be used if all three are on the same type of base, receive the same treatment in processing, and are dried slowly and uniformly while oriented in the same manner. The emulsions on film are generally much more evenly coated than on the same size plate and less difficulty is experienced from local color irregularities due to such unevenness.

The material used in the various tricolor cameras is generally prescribed by the camera's manufacturer so that a balanced set of color records is obtained. For a given set of mirror conditions and color temperature of incident light, the negatives give equal gray scales with proper development. Any alterations in the color temperature of the light being used, the characteristics of the supplied emulsions or the conditions of development will necessitate some form of compensation to secure balanced negatives again. When a single mirror camera employing a bipack is used, the design is built around some commercially available emulsion material and its use is essential for a satisfactory balance in the three separation negatives.

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[2] Houskeeper, *Phot. Tech.* **2** (1940) No. 2, 26. Colton, *Phot. Tech.* **2** (1940) No. 7, 54. Coote, *Brit. J. Phot.* **87** (1940) 15.

Lighting in Color Photography.—In tricolor photography, both the quantity and quality (color temperature) of the illumination are of great importance.

The quantity of illumination required in color photography is generally somewhat greater than that necessary for black and white work due to the light losses involved in the exposure of the sensitive materials. The quantity of illumination must also be considered in respect to the different areas of the picture. Color processes are more limited in regard to exposure latitude than black and white and therefore precautions should be taken to avoid dark pockets which might reproduce as colorless holes. Subject matter of unduly varying luminosity and color may require some adjustment in the relative quantity of illumination since a fairly dark green and a bright red cannot be given any single exposure under constant illumination that will show them in the proper ratio in a modern color transparency. Separate illumination is often necessary to bring the various hues and values in the subject up to light levels that will give a satisfactory reproduction. The judicious use of an exposure meter is indicated for accurate color work.

In black and white photography, the modeling and contrast are supplied by the subject matter and its lighting. In color photography a great deal of both is supplied by the color of the subject. It is therefore unnecessary, indeed unwise, to use lightings of very high contrast for color photographs unless special effects are desired. Harsh highlights tend to be devoid of color and poorly illuminated shadows will be black. The lighting should be more like what is termed soft, although not necessarily flat.[3]

The second attribute of illumination, its quality, is of very real importance to the color photographer. Commonly used light sources differ widely in their energy distribution through the visible spectrum

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[3] Haskell, *Camera Craft* (1938) 110; (1940) 550, 601. Baker, *J. Soc. Mot. Pict. Eng.* **29** (1937) 471.

(see Chapter V). Daylight, because of its variations, is not the best source for color photography. Some sort of artificial light is a better choice. Suitable light sources for color work are shown below:

Daylight floods and flesh lamps	5600° K.
Arcs (H.I.)	5100° K.
Flash (clear lamps)	3300–4000° K.
Photofloods	3300–3450° K.
High intensity tungsten lamps	3000° K.

The type of light source employed is of little importance as long as (1) the various color records are balanced for the chosen color temperature, and (2) the various light sources are all of the same color temperature (exceptions for special effects). Reasonable precautions in regard to reflected light, lamp reflectors and diffusers should be employed. The use of a color temperature meter [4] for testing illumination is quite helpful. The light source should emit radiation in each region of the visible spectrum without sizable dark regions or pronounced bright lines. Sources of the latter two types, while quite usable, will occasionally give false color rendition of certain hues affected by the uneven spectral distribution.[5] All possible precautions should be taken to hold the color temperature of the illumination constant at a predetermined value. The use of voltage regulation is advisable in most locations as very small fluctuations in line voltage lead to large changes in the color temperature of the emitted light.[6]

Lens.—A good color-corrected anastigmat should be used for making three-color negatives; other lenses may not produce images of the same size or sharpness on all three negatives. For the highest quality work where accurate registration, even on a sizable enlargement, is necessary, the use of an apochromat is advisable (see Chapter II).

The color filters chosen should not impair the definition of the lens. For the longer focal lengths, optically flat filters or gelatin sheets must be employed.

The use of a lens hood is advisable to minimize the effects of scattered light or flare, especially with the tricolor camera.

Reference Object.—It is helpful to include in the scene a reference object consisting of a scale of gray tones. This reference object is useful (1) to insure proper balance of both density and contrast in the three separation negatives, and (2) to aid in the determination of positive exposure times and judgment of the best print quality. The reference object should consist of a scale of gray tones from white to black and each step should be large enough on the negatives to be read in a densitometer. The density range of the gray scale should preferably include all densities present in the subject in which accurate color reproduction is desired. The gray scale should be placed in the picture area so that it will receive the same illumination as the important parts of the subject. Any variation in the illumination will lessen its value as a reference object. The gray scale should appear on the separation negatives somewhat away from the edge to avoid any emulsion variations along the margins of the negatives. For small objects, the Wratten copyboard chart forms a convenient reference object. In addition to a scale of grays, it contains registration lines and color patches to aid in the identification of the three negatives after development. When larger scales are required, such as in outdoor work, a suitable scale of grays may be made by exposing sheets of developing-out papers and developing so as to obtain a neutral black deposit. The number of steps may vary from two, a white and a black, up to about ten. The more steps available, the more complete, useful and accurate the information provided.

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[4] Lowry and Weaver, *J Soc. Mot. Pict. Eng* **32** (1939) 298.

[5] Sources such as Fluorescent Tubes and Kodatron Speed Flash Lamps fall into this category.

[6] Forsythe, *Phot.Tech.* **1** (1939) No. 6, 20. Dudley, *Phot.Tech.* **1** (1939) No. 10, 8.

Filter Factors and Exposure.—The filter factors for color separation negatives show the amount of exposure increases necessary for the various filters to produce negatives in which the reference gray scale will be of the same densities as in a negative exposed without any filter. With a panchromatic material, the filter factors for the set of three-color filters approved by the manufacturer are determined by test for each emulsion number and printed on a card which is packed with the films or plates. While these values are accurately determined, they should not be accepted as final, since the factor of a filter depends upon a number of considerations (see p. 462) for which it is difficult to make allowance. Slight alterations in the color temperature of the light source, development to different gammas or even the age of the sensitive materials might necessitate a minor revision of the filter factors. The standard tricolor filters of a single manufacturer are not exactly alike as to their transmission, and filters should be kept together in sets and the exact factors checked with the filters to be used in practice.

Eastman Kodak Co., Photography of Colored Objects, Chapter IX.

For all but the most precise work, it is sufficient to make a set of trial exposures under similar conditions to those to be employed later, using the factors submitted with the sensitive material. When properly developed, the gray scales on the three separation negatives may be compared visually or with a densitometer. Suitable exposure and development adjustments are then made, if necessary, to insure that the scale densities are alike on each color record. For most types of work, it is of greater importance to have the negatives match in contrast rather than in density, but if the subject is one of a rather long brightness range, the densities should be matched as closely as possible. Any deviation from equivalence will make some colors record beyond the correct reproduction region of one of the emulsion's characteristic curves and inaccurate color reproduction will result. For the most precise work, account must be taken of the failure of the reciprocity law and the filter factors determined under the proper exposure conditions.[7]

Development.—It is important that the three color separation negatives have not only approximately the same density levels but also that their contrasts be alike so that each step on the gray scale of one negative finds an equal density on the other two negatives for the same step. Contrast for color separation negatives is generally indicated by the term "density range" rather than "gamma." The density range is simply the difference in density readings of the black and white portions of the gray scale reference chart, assuming that the chart range includes all densities present in the subject.

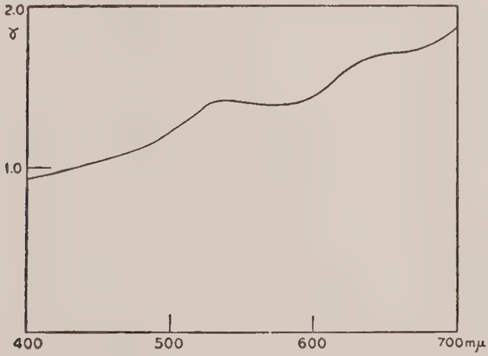

FIG. 366. Wave-Length-Gamma Curve for a Typical Panchromatic Emulsion

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[7] Tupper, *Phot.Tech.* 2 (1940) No. 5, 29.

Due to the gamma-wave length characteristics of the photographic emulsion, it is generally necessary to develop the three separation negatives for different times to obtain satisfactory balance. Panchromatic emulsions have lately appeared in which the gamma-wave length variation is relatively slight but it is not uncommon to have to increase the development for the blue separation record about fifty per cent over that necessary for the red and green records. A typical wave length-gamma curve for a panchromatic emulsion is shown in Fig. 366. The variations in developing time must be borne in mind when determining the filter factors for the three color records. A given panchromatic emulsion may also show varying shaped characteristic curves when exposed to radiation of different wave lengths. This unfortunate condition may only be overcome by the choice of appropriate emulsions and developers.

The contrast to which the negative should be developed depends upon the procedure to be used in making the three-color print. If the printing process increases contrast, the contrast of the negatives must be correspondingly lower, while if the contrasts obtained in the positive stage are low, then the negatives must be developed to a higher degree of contrast. In general, soft, well-graded negatives with slightly less contrast than would be employed in black and white work are desirable. A successful set of negatives depends to a large extent on the care taken in developing. Uneven development will result in color patches when the negatives are printed, and it is practically impossible to cover up such deficiencies in the printing. Since the eye is much more sensitive to variations in color than it is to variations in black and white, extreme precautions must be observed to avoid any unevenness.

It is advisable to develop separation negatives in a developer that gives a neutral image deposit, since (1) a colored image would have a somewhat different visual and photographic contrast, and (2) negatives that may later be masked with other negatives or positives should have neutral images on both emulsions to avoid anomalous sensitometric curves when used together.

Development may be carried out in either a tray or a tank. In the latter case, it is essential that each image be oriented the same way to avoid color wedging. In tray development, a rather large volume of solution should be used in a tray at least one size larger than the negative being developed. Local variations in development are difficult both to avoid and to trace to their source. Continuous irregular agitation or brush development is advisable unless automatic developing machines are employed.[8] Negatives developed under varying conditions of agitation may show a series of sensitometric curves similar to those found upon small variations in developing time (Fig. 367). Precautions must also be taken to keep the temperature of the developer constant to within ± 1° F. since small temperature changes give very decided differences in negative contrast. To help keep development conditions constant, it is advisable to use a fresh volume of developer solution for each color record or set of separations. The importance of satisfactory negative balance and even development cannot be over-emphasized as the success of the color print is entirely dependent upon the quality of the separation negatives used to produce it.

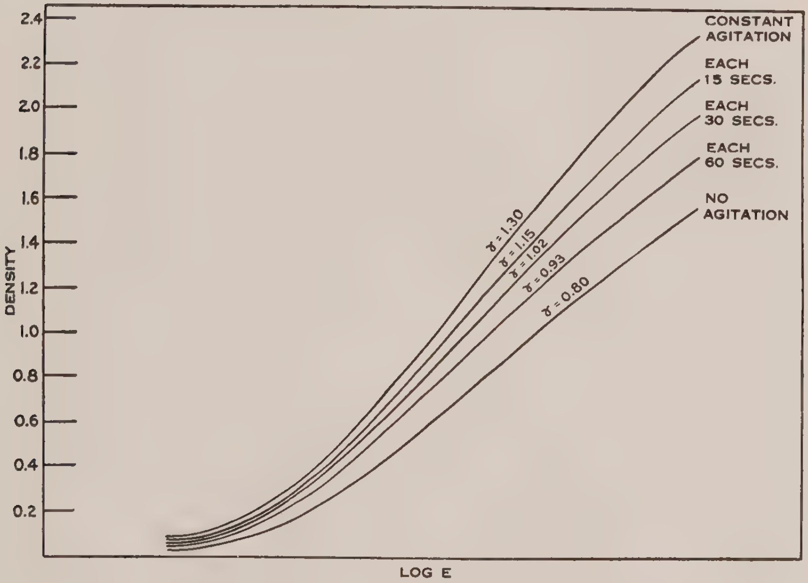

FIG. 367. Change of Gamma with Agitation (Agfa Diamond).

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[8] Clark, *Phot.Tech.* 2 (1940) No. 10, 54.

CHAPTER XXXI

SUBTRACTIVE PRINTING PROCESSES

Introduction.—Additive systems of color synthesis have several advantages over the subtractive synthesis used in the common three-color paper reproduction processes (see Chapter XXXII). The additive processes are not suitable, however, for prints on paper and are therefore of little practical interest to the professional photographer. Even in motion picture work, the difficulties with additive processes in projection and cost make the subtractive printing methods of more general commercial interest.

Types of Subtractive Printing.—All three-color subtractive processes use the colors cyan, magenta and yellow in printing from the red, green and blue separation negatives. The exact shades of cyan, magenta and yellow used in the various processes varies widely, although the ideals would be optically equivalent to the additive synthesis colors. The cyan and magenta are the poorest colors and are often, in reality, blue and red. The color of most yellow print mediums is quite satisfactory. The procedure for all subtractive processes is to superimpose in register the three colored positive images made from the appropriate color separation negatives. A classification of photographic subtractive printing processes on the basis of their method of forming the colored images shows six distinct types of processes. The lines of demarcation between the various methods cannot be drawn too clearly since some commercial processes are in reality combinations of the basic types listed. This chapter will be devoted to a discussion of the various processes involving the superimposition of three positives to produce the final print, leaving integral tripacks for a following chapter.

Metallic Toning.—The three-color toning processes make use of the principle common in producing colored pictures in monochrome—the replacement of the black silver image by an image of another metallic compound which gives the desired color. The procedure for three-color prints is similar, although more complicated, to that employed in obtaining a sepia print by redevelopment. Successful three-color metallic toning processes are relatively new in color photography because (1) a satisfactory magenta color has not been obtainable until

SUBTRACTIVE PRINTING PROCESSES

Process	*Image Material*
I. Toning Processes	
A. Metallic Toning	Colored Metallic Salts
B. Dye Toning or Mordanting	Dyes, usually basic
II. Gelatin Relief Processes	
A. Tanning Development	Dyes or Pigments
B. Dichromated Colloids, Hardening Brought about by:	
1. Light	Pigments
2. Silver	
a. Carbro	Pigments
b. Hardening Bleaching	Dyes
c. Dyebro	Dyes
C. Etching	Dyes
III. Differentially Hardened Colloids—relief formation not essential	
A. Differential Staining	Dyes
B. Differential Water Absorption	Inks
IV. Dye Coupling	Dyes
V. Dye Destruction	Dyes
VI. Dye Bleaching	Dyes

recently, and (2) a satisfactory balance of density and contrast in the three images was difficult to obtain.

A satisfactory metallic cyan image has been available for some time in the standard iron toning baths. Many variations of this toner have been in common use, especially for two-color motion picture processes and for making blue toned prints in monochrome photography. Yellow images are readily obtainable by the conversion of a silver image to yellow lead chromate, cadmium sulfide, or nickel ferricyanide. Of these three the first two produce the best hues. The search for a satisfactory magenta metallic image was fruitless until 1930. Between 1930 and 1936, several British and United States patents were granted for obtaining the magenta images with Nickel Dimethyl-glyoxime or *p*-dimethylamino-benzylidenerhodanine. Previous toning methods had made use of uranium and copper toners which, while rather useless for three-color photography, were quite successful in two-color processes since the image color was red rather than magenta.

With the devolpment of a satisfactory magenta toner, the remaining difficulty was in the compounding of the three toners so that satisfactory density, contrast and control were available for each color. The successful conclusion of this investigation and the introduction of a con-

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Chromatone Process, Defender Photo Supply Co., Rochester, N. Y.

venient positive stripping film on a removable paper support prepared the way for the launching of a commercial toning process of three-color photography by the Defender Company, under the name of Chromatone.

In brief, the Chromatone process necessitates the making of three black and white positives on a special collodion stripping paper. Considerable opportunity for the control of contrast is afforded by variations in the processing of the positive images. The stripping paper is available in two grades of contrast and several developers are suggested. Exposure and development are altered until equal gray scale neutrals are obtained on each of the three positives. After development, the three positives are fixed in a non-hardening fixing bath and washed thoroughly before toning. During washing, the water soluble adhesive layer securing the emulsion coated collodion to the paper base is softened enough to permit the removal of the image-bearing collodion film from the paper backing, which is discarded. The three positives are next toned to the proper colors. The magenta is obtained by bleaching in a bath of a nickel salt, potassium ferricyanide, and various other reagents to control the conversion to nickel ferrocyanide. After washing, the white image is then converted to nickel dimethyl-glyoxime and treated with hypo to remove the silver ferrocyanide, the desired transparent magenta image remaining. The cyan image is obtained in a similar manner, being converted to an iron instead of a nickel compound. The yellow image is obtained by bleaching in a lead nitrate bath to lead ferrocyanide and then converting to yellow lead chromate. Precautions must be observed in carrying out the toning to avoid the possibility of contaminating one solution with another. After toning and a final washing, the three colored films are ready for assembly. If necessary, a slight reduction in the intensity of the various images may readily be made since the yellow and magenta images are somewhat soluble in acid and the cyan in alkali. Caution must be exercised in controlling any such reduction since the highlights are reduced rapidly, and all alkali and acid must be removed before the films are assembled. The yellow image, being the most opaque of the three, is squeegeed to a wet gelatinized paper and the other two superimposed in register, the whole assembly being taped to a glass support and dried. The surface of the print may be altered during assembly or before mounting.

Dye Toning.—The dye toning process involves the replacement of the positive silver image by a compound having an affinity for dyes. These methods are sometimes called dye mordanting processes since the compound replacing the silver image acts as a mordant for the coloring matter. The most commonly used mordants are silver iodide, several metallic ferrocyanides and sulfocyanates as well as various complex compounds composed of two or more substances of the above types. Mordants for color photography should, of course, be as transparent and colorless as possible, and several of the above mentioned possibilities are satisfactory.

In general, basic dyes are more readily attached to the available mordants than the acid dyes and are used for most dye toning. The usual procedure is to make three thin, low contrast positives on film and then, after fixation and washing, treat them with the chosen mordanting bath. After the silver image is converted to the mordant, the films are washed and dyed in weak solutions of the appropriate basic dyes. A final washing clears the non-image portions of dye. The three images are then registered either as a transparency or stripped from their supports and superimposed to form a print on a white support.[1]

The dye mordant processes are capable of yielding highly accurate color pictures due to the brilliance and desirable hues of the basic dyes. The chief disadvantages of processes of this type are the difficulty in holding clear whites and the lack of permanence of the dyes used. Little commercial color photography is practiced today with the dye toning processes.

Relief Processes.—Several methods of making color photographs may be classed as relief processes. A relief process is one in which, instead of an image composed of silver in gelatin, there is a layer of material, usually gelatin, of variable thickness—the thickness being varied in the same manner as the quantity of silver in the usual print. It might be said in describing such a film that instead of having a variable density (silver image), it has a variable thickness (gelatin relief image) (see Fig. 368).

Under the heading of Relief Processes are included two of the most common paper color print processes—Carbro and Relief Imbibition. The cross mixtures of relief formation and coloring materials testify to the thorough search that inventors have made for practical methods of making color prints. Thus, there are relief processes in which the relief is colorless gelatin, which is later dyed, the final print being made by imbibition, and those in which the reliefs are permanently colored

[1] Friedman, *Amer. Phot.* **32** (1938) 209; **35** (1941) 145, 210, 302.

with pigments which themselves compose the final image. The production of the relief itself, no matter how used later, may be carried out by a variety of methods as indicated in the process classification table.

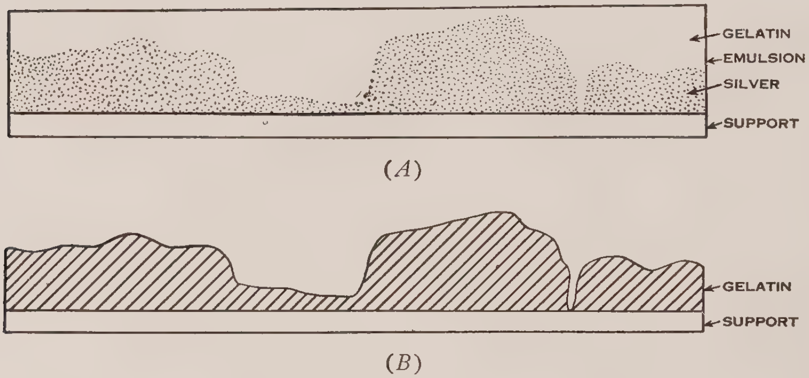

FIG. 368. A Normal Photographic Image (*A*) Composed of Silver Grains Which Give the Photographic Density. A Similar Relief Image of Gelatin (*B*) May be Clear or Contain Some Coloring Material.

Tanning Development.—Gelatin relief formation by means of tanning development depends on the fact that the oxidation products of certain developing agents, notably pyrogallol, pyrocatechin and hydroquinone, exert a tanning action on gelatin. This reaction occurs wherever the silver image is formed, the remainder of the gelatin being unaffected. The tanning action depends on the composition of the developer. Preservatives such as sodium sulfite retard the oxidation of the developer and if present in large enough concentrations may prevent any tanning of the gelatin. Most formulae compounded for tanning development contain a minimum or no preservative. A typical developer, for example:

Solution I

Citric acid	16 gm.	234 gr.
Pyrogallol	140 gm.	4¾ oz.
Ammonium Bromide	40 gm	1 oz. 147 gr.
Water to make	1 liter	32 oz.

Solution II

Sodium Hydroxide	30 gm.	1 oz.
Water to make	1 liter	32 oz.

Take one part each to 25 parts of water. Develop 5 minutes at 18° C.

The production of gelatin reliefs by means of tanning development must be carefully standardized since the insolubilization of the gelatin goes on after the film is removed from the developer. A constant wash followed by fixation and bleaching is carried out before the removal of the unhardened gelatin by hot water.

The Duxochrome process for color prints makes use of a tanning developer, pyrocatechin, in the production of three relief films. The Duxochrome films are sensitized with the usual silver halides but in addition contain coloring pigments suspended in the gelatin. These films, colored cyan, magenta and yellow, are exposed through the film base to the proper negatives and developed in the tanning developer which tans the gelatin wherever silver halide is reduced. The films are then developed in hot water which dissolves the soluble gelatin and bleached in a reducer to remove the developed silver. The colored gelatin relief positives may then be placed in register for a transparency or dried in succession onto a paper base to make a paper print. This process allows considerable latitude and control of the various color images but has never been very popular in the United States. The pigments composing the final image are not so brilliant as dyes and are somewhat grainy.[2]

Reliefs made by tanning development have also been used widely for imbibition dye printing. The Technicolor Corporation made many colored motion pictures by printing from such matrices. The hardness of the relief after suitable tanning development is an important factor where many successive printings are desired from a single set of matrices. Matrices prepared in the above manner may therefore be used for color printing on paper by the imbibition process as successfully as reliefs made by dichromate hardening solutions.

Hardening Action of Light on Dichromated Colloids.—One of the most important photographic reactions is the hardening[3] action of light on dichromated colloids, discovered by Ponton in 1839. The photo-mechanical processes as well as strictly photographic procedures make continual use of this reaction. The colloid used in color photography is always gelatin which may be either clear or contain some coloring pigment in suspension. If such a gelatin film is bathed in a solution of a dichromate and dried in the dark, it becomes light sensitive. When exposed under a negative to a strong actinic light the gelatin becomes insoluble in proportion to the intensity of the exposure. If the film is placed in warm water, the unaffected gelatin may be dissolved and removed.

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[2] *Phot. Ind.* **38** (1940) 558.

[3] For the purposes of color photography, tanning and hardening give the same result—the insolubilization of the gelatin. Strictly speaking, tanning is a reversible reaction while hardening is not reversible. Grutzne, Gelatine-Leim und Klebstoffe, Jan. 1939.

The Carbon process, which has largely been superseded by carbro, employed this procedure for making three-color prints. Belcolor and Dufaytissue are modern adaptations employing the same basic reactions with new technique and materials. In general, both of the last processes are alike in that pigmented gelatin films are sensitized in bichromate solutions and dried in the dark before exposure to the proper separation negatives. After exposure through the film base under strongly actinic light, the films are developed to reliefs in hot water.[4] Some local control may be exercised with very hot water in areas requiring reduction. When a satisfactory balance is secured the films may be dried. The three colored films may either be combined to form a transparency (if the contrasts are sufficiently high) or the films may be superimposed on paper to form a paper print. By using a suitable cement, the pigmented gelatin may be secured to the paper and the transparent films removed. As transparencies, these processes have found wide acceptance in the graphic arts fields for use as color guides because of the simplicity and rapidity with which they can be prepared.

Hardening Reaction between Silver and Dichromated Colloids.—The result considered in the previous section may be duplicated in a simple manner by means of a reaction discovered by Howard Farmer in 1899. If a developed image consisting of finely divided silver is treated with a suitable dichromate solution, the gelatin surrounding the silver grains is hardened in a manner similar to the hardening of a dichromated colloid by light. This interesting reaction is the basis for two of the most widely used color processes, relief imbibition printing and carbro printing. In appearance these two processes are dissimilar but in reality they are dependent on a similar chemical reaction. The exact reactions are not known but it will suffice to say that the dichromates are reduced and one or some of the reaction products are capable of hardening gelatin. In the relief imbibition process, the hardening action takes place around the individual silver grains while in the case of carbro the hardening action is transferred to an adjoining layer of gelatin. In both processes the unaffected gelatin is washed away with hot water, leaving a positive relief image of gelatin. In imbibition printing the relief is of clear gelatin which is later dyed, the dyes being transferred to a paper base. In carbro, the gelatin reliefs contain pigment and the final print is composed of a combination of the three pigmented relief images on a single paper support. As these two processes are widely used for commercial and amateur color printing, it would seem advisable to review briefly the procedures employed.

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[4] Beale, *Phot. J.* **81** (1941) 108.

Relief Imbibition Printing.—The introduction in 1934 of Wash-off Relief film by the Eastman Kodak Company and their presentation of an outline of procedures made the relief imbibition process generally available. This method of color printing was not new, but satisfactory materials for its practice were not previously obtainable. Since the publication of the method under the name of the Eastman Wash-off

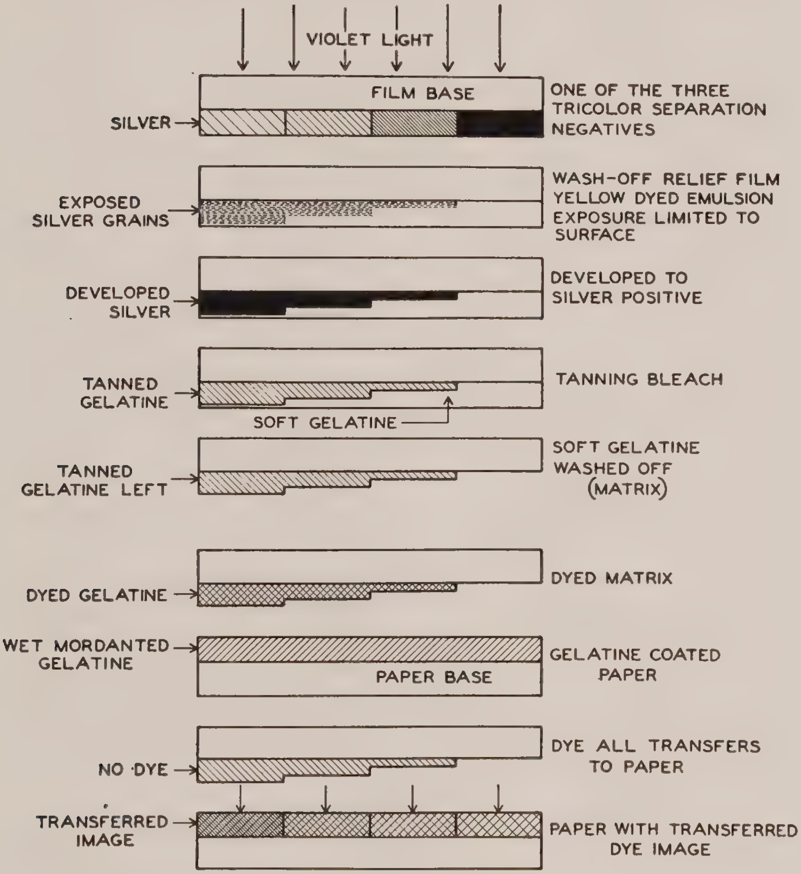
VIOLET LIGHT
FILM BASE
SILVER
ONE OF THE THREE TRICOLOR SEPARATION NEGATIVES
EXPOSED SILVER GRAINS
WASH-OFF RELIEF FILM YELLOW DYED EMULSION EXPOSURE LIMITED TO SURFACE
DEVELOPED SILVER
DEVELOPED TO SILVER POSITIVE
TANNED GELATINE
TANNING BLEACH
SOFT GELATINE
TANNED GELATINE LEFT
SOFT GELATINE WASHED OFF (MATRIX)
DYED GELATINE
DYED MATRIX
WET MORDANTED GELATINE
PAPER BASE
GELATINE COATED PAPER
NO DYE
DYE ALL TRANSFERS TO PAPER
TRANSFERRED IMAGE
PAPER WITH TRANSFERRED DYE IMAGE

Fig. 369.

Color Printing with Eastman Wash-off Relief Film—Eastman Kodak Co.

Relief Process, other manufacturers have introduced similar blue sensitive as well as panchromatic emulsions for relief production and dyes for printing, along with several minor modifications of procedure (Fig. 369).

Making the Reliefs.—The Relief films available are fine grained positive emulsions having speeds similar to fast projection papers and are a development from duplicating film. The emulsion is dyed yellow during manufacture with a dye such as tartrazine which is removed during processing. Exposure by contact or projection is made through the film base to keep the entire latent image in contact with the support so that the relief image will remain attached to the film base when "developed" in hot water. The contrast of the positive may be controlled by altering the color of the exposing light since the opacity of the yellow colloid is greatest for blue light and least for yellow light. Use may also be made of the emulsion's inherent variation of contrast with the wave length of the exposing light. A series of filters such as violet, blue, blue-green and yellow-green will give images of increasing contrast after compensation is made for the exposure increases required by the differently colored exposing lights. A rough approximation to the exposures may be found by using a projection paper of similar speed. For development, a number of developers have been recommended ranging from the soft DK20 up to a contrast developer such as D11. The addition of small quantities (two grams per liter) of potassium thiocyanate to a normal developer leads to slightly lower contrast of the relief image, especially in the highlights. Processing may be carried out in trays or in film hangers in a tank. After development, the films are thoroughly washed to stop development and remove all traces of the developer, especially the sulfite. When washing is complete, the films are bleached in an acid bichromate bath containing a halide salt such as Kodak Formula R–10a. A small volume of bleaching solution

Stock Solution I			*Stock Solution II*		
Water............	500 cc.	16 oz.	Sodium Chloride..	45 gm.	1½ oz.
Ammonium Bichromate............	20 gm.	290 gr.	Water to make...	1 liter	32 oz.
Sulfuric Acid C. P...	4 cc.	1 dr.			
Water to make......	1 liter	32 oz.			

For use take
1 part Solution *A*
1 part Solution *B*
6 parts water

should be mixed shortly before use in a tray and then discarded. If the films are processed in hangers, using deep tanks, a mixed bleaching bath may be used about four hours before being discarded. The final stages of bleaching and subsequent processing steps may be carried out in bright light. The bleaching of the silver image is accompanied by the hardening of the gelatin by the reduced chromic salts. The silver is converted to silver chloride. When all of the silver is bleached, the films are "developed" in hot water (52° C.) to remove the unhardened gelatin. As the hardening reaction only occurs at positions containing a silver image after exposure and development, the layer of gelatin remaining after the hot water treatment shows as variations in thickness what the silver image formerly showed as density. When all the soluble gelatin has been removed, the films are cleared of the remaining white silver halide by immersion in a plain or hardening acid hypo solution. The relief "development" may also be carried out in cool 20% solution of ammonium thiocyanate which not only removes the soluble gelatin but also fixes the remaining silver halides. The solution may be stored and used repeatedly. The films are then thoroughly washed, briefly hardened in a solution of formalin, and dried. The three films are now ready for dyeing in the appropriate dyes. If desired, the faint brownish gelatin stain may be removed by a permanganate bleach. The removal of the stain makes judgment of the color balance before printing somewhat easier and improves the clarity of films to be bound together for use as a color transparency.

The judgment of the correct exposure seems to be one of the more difficult steps in imbibition dye printing. The most accurate results are secured by dyeing the reliefs and examining the three together or each one individually as seen through the complementary colored filter. The judgment of exposure may also be made by viewing the relief film directly after the hot water development but before fixation. At this stage, the highlights should be slightly veiled—only experience will tell the exact amount. For consistent results, the processing of relief films should be standardized as thoroughly as possible and development times and temperatures strictly adhered to.

Many variations on the procedure of matrix making have been published. For example, a stop bath of acetic acid may be used directly after development followed by a shorter washing, or the films may be fixed and dried before bleaching. Panchromatic relief emulsions are dyed black and exposures may be made from integral color negatives through tricolor filters. The exact procedure followed is not of vital importance so long as the manipulation is satisfactory and reproduceable. Various procedures are available from the dye or film manufacturers and should be consulted before making the matrices.

Dyeing the Reliefs.—The dyes used for imbibition printing are generally of the acid type and their choice is quite critical as regards their hues and transfer characteristics.[5] The dyes may be prepared by the user or packaged products are commercially available that have been especially prepared for imbibition relief printing. Whatever dyes are used the matrices are placed in the proper dye solution until absorption is complete and then the excess surface dye is rinsed off with dilute acetic acid. The sole purpose of the acid rinsing is to remove all surface dye and prevent any bleeding of the dye from the gelatin relief image. The acid rinse bath should be of as low a concentration as will keep the dye from bleeding, generally about one-half per cent acetic acid. Transfer of the three images is carried out by printing the slowest transferring dye first and the most rapid dye last. As the rapidity of transfer of any given dye is retarded by an excess of acid on the paper, the lower the necessary acid content of the rinse baths, the more rapid the dye transfer. The thickness of the relief is another controlling factor in the rapidity of transfer and the most rapid transfers are obtained by using soft low reliefs and dyes of considerable acid content to give the desired contrast, rather than contrasty thick reliefs and low acid content dyes. Both heat and pressure tend to accelerate dye transfers. Rapid dye transfers also give a print showing the maximum possible definition since image bleeding increases with the time interval between dye absorption and drying.

The quantity of acid added to the dye solution controls the absorption and therefore the contrast of the dye image. Prepared dye products are generally arranged so that equal additions of a weak acetic acid solution to each of the three dyes will give equal increase of contrast. It is rarely true that the three dyes will stay in balance over a sizeable range of contrasts with equal additions of acid and the best print is not necessarily obtained by having the same quantity of acid in each dye bath—assuming the relief images are made from negatives which were originally in balance.

One of the most useful characteristics of imbition printing processes is the ease with which slight variations of density and contrast may be made after the printing positives are prepared. A reduction in the density of any one or all of the colored images is possible by washing the matrix down slightly in plain water. When the desired reduction has taken place, the film is returned to the acetic acid rinse bath. Alterations in contrasts are also readily made either by increasing or decreasing the acidity of the dye baths.

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[5] Friedman, *Amer. Phot.* **34** (1940) 529, 609. Colton and Thronson, *Phot.Tech.* **2** (1940) No. 11, 54.

The actual dye transfer is made onto a prepared gelatin surface. The gelatin is generally treated with a mordanting solution which provides a medium with an affinity for acid dyes and helps prevent spreading of the image in the gelatin. The gelatin surface may be either ordinary photographic paper which has been fixed or it may be a plain gelatin surface on a paper, film or glass support. Aluminum hydroxide is a typical mordant for acid imbibition dyes. The acidity of the gelatin layer must be carefully controlled for efficient transfer of the dyes, and buffer solutions may be employed in connection with the mordanting operation to leave the gelatin surface at the proper pH.[6] Imbibition printing papers that have been mordanted are also available commercially. Whatever material is used, it must be carefully expanded in water before any transfers are made and must be kept moist during the dye transfers. As there is some slight diffusion of the dye images after they are in the paper, it is advisable to dry the print as quickly as possible after the transfers are completed. A very slight increase in contrast and change of hue occurs with most dyes when dried but the alteration may be compensated for before transfers are begun.

For a limited number of prints, the registration of the three images may be done during the printing operation by using a thin layer of film base between the dyed relief and the prepared gelatin surface. When register is obtained, the film may be removed and the relief squeegeed into intimate contact with the transfer surface. For quantity production, the relief films may be perforated along the margins and registered mechanically on the transfer board supporting the transfer paper. In fields requiring a number of successive pictures, the relief imbibition method is most practical. With moderate care, the relief films are capable of producing a series of duplicate color prints. For work of this nature, dyes are chosen having very short transfer times and registration is done automatically. Due to the abrasion of the gelatin reliefs and their absorption of various ingredients from the transfer papers, the number of acceptably comparable prints is limited to approximately one hundred and fifty per matrix.[7]

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[6] *Brit. J. Phot.* **86** (1939) 435; **87** (1940) 611.

Three-color Carbro.—The Carbon process was for a long time the only really practical means of printing from three color negatives. In recent years, it has largely been superseded by three-color carbro. Three-color carbro, while more exacting in its technique than other processes in general use, in capable hands is still unsurpassed. The procedure, in general, is the same as monochrome carbro (see Chapter XXV) except that three color pigments are employed and several image transfers are required.

Bromides.—The basis for a satisfactory three-color carbro rests on the bromide prints made from the color separation negatives. The emulsions employed are usually specifically coated for carbro printing and do not have the gelatin anti-abrasion overcoat generally placed on sensitive photo papers. The emulsions are of the fast projection type and are obtainable both in cut sheets and rolls. Care must be taken to have the paper grain run in the same direction on each print of a color set to avoid unequal expansion and later registration difficulties. The cut sheets available for carbro come with the same grain orientation throughout a package.

The production of a three-color carbro print does not offer as much opportunity for photographic corrective measures as is available in relief imbibition printing. The two stages where corrections can be made, however, offer enough variations to enable considerable adjustments to be made. The bromide printing step offers the first and most reliable stage of control in that variations of both density and contrast of any or all three images may be carried out during exposure and development. Exposure determinations are generally made from the cyan printer. The safest criterion is a slight veiling over of the highlight portions of the image corresponding to subject areas containing little or no cyan color. A gray scale, if properly illuminated when the subject was exposed, may also be used. When a tentative exposure has been determined for the cyan printer bromide, the magenta and yellow printers are exposed and developed so that identical gray scales are obtained on each print. Such a result will be obtained with equal exposures and developments, given negatives of equal densities and density ranges. If the maximum density varies, compensation of exposure may be calculated from the density readings. If the contrasts of the three separation negatives are different, all possible steps should be taken to make the contrasts of the positive images identical. Considerable variations are feasible by making use of variable contrast developers or using two or three different developers (Fig. 370). The use of a reflection densitometer is quite helpful but not essential as scales on paper may be quite accurately compared visually. The inclusion of a gray scale in the original scene is of inestimable value when corrective work is necessary.

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[7] Colton, *Phot.Tech.* 3 (1941) No. 11, 20.

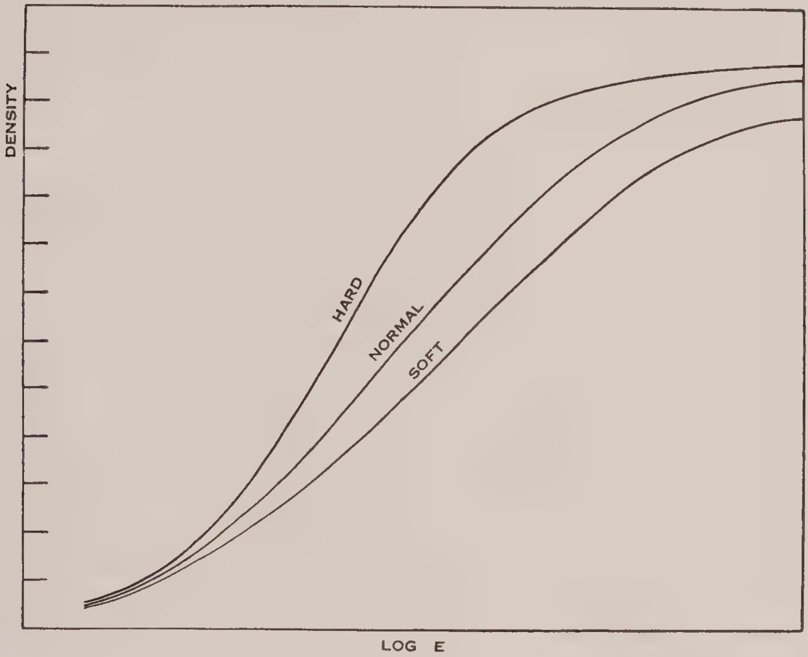

Fig. 370. Contrast Variations Obtainable with Various Developers and a Common Carbro Printing Paper.

Development must be carefully standardized as to time and temperature to make possible reproduceable results. Slight variations that would be of no importance in black and white will give an unsatisfactory color print. An acid stop bath rinse is advisable for the bromides followed by fixation in a non-hardening fixing bath. With occasional agitation in a fresh fixing bath, five minutes fixation should be sufficient and all prints should be treated alike. A thorough wash in water, at least an hour, will leave the bromides ready for pigment printing. The acidity of the paper determines to some extent the density of the pigment image obtained from a given bromide. Since wash water varies in alkalinity at various locations in the country, it is advisable to bring bromides to a definite pH value after washing. A number of buffer solutions may be prepared which will enable the operator to hold the bromides to the desired pH value. A value of roughly 6.5 seems to be a happy medium. The bromide prints, after washing, are swabbed off with a 2% acetic acid solution to remove any surface alkali. Afterwards they are briefly washed and then brought to the proper pH value by soaking in a tray of appropriately buffered water. The bromides are then ready for pigment printing or they may be dried before use. If dried, the prints must be suspended from two corners and all oriented in the same manner.

Preparing the Celluloids.—The sheets of celluloid on which the pigment images are developed should be at least 2 inches larger in each direction than the prints and about 1/50 of an inch thick. After cleaning with turpentine, one surface of each celluloid is waxed with a special waxing solution and a polishing pad of lintless cloth. The celluloids must be fully covered with a minimum of wax and polished until no more can be removed. An excess of wax will lead to frilling of the pigments during development and insufficient wax will lead to difficulty in removing the pigment images from the celluloid.

Sensitizing.—The sensitizing solution for soaking the pigment papers may take several forms both as to constituents and their division into separate baths and combinations. The most widely used sensitizers are combinations of bichromate, bromide and ferricyanide, although copper chloride is sometimes used. There has been a decided tendency to adopt the single bath procedure in recent years and such a sensitizing formula is given below:

Stock Solution I		
Potassium Ferricyanide	50 gm.	1 oz. 293 gr.
Potassium Bromide	50 gm.	1 oz. 293 gr.
Ammonium Bichromate (A. R.)	15 gm.	219 gr.
Water (not over 75° F.) to	1000 cc.	32 oz.
Stock Solution II		
Chromic Acid Flakes	10 gm.	146 gr.
Water to	1000 cc.	32 oz.
Stock Solution III		
Formalin	50 cc.	1.6 oz.
Water to	1000 cc.	32 oz.

Tricolor Pigment Printing, Devin-McGraw.

Making Color Prints with 3 Color Pigment Paper, National Photocolor Corporation.

For use take 200 cc. of Solution I, 100 to 150 cc. of Solution II, and 10 to 20 cc. of Solution III. The exact quantity of stock solutions used depends somewhat upon the pigment paper employed, and the manufacturers should be consulted for the best combination to employ with the paper in use.

The second possibility of control occurs in the use of the sensitizing bath, although worthwhile variations of contrast are considerably less than those obtained in the development of the bromides. The quantity of No. II stock solution used determines the contrast of the pigment image, the smaller quantities giving the most contrasty result.

The pigment papers, cut slightly larger than the bromide prints, are first soaked in cold water until they become limp, and then placed in the sensitizing solution in the order of cyan, magenta and yellow. The sensitizer should be kept around 18° C. to prevent excessive swelling of the pigmented gelatin. Each pigment stays in the sensitizer for three minutes and they are therefore removed in the same order at one minute intervals. When the cyan pigment is ready to be removed, the bromide print is placed on a glass plate and covered with a pool of water and the sensitized pigment paper is lowered onto it and rapidly squeegeed into contact to remove all water and air between the two surfaces. This sandwich is then laid aside. The same operations are then carried out for the magenta and yellow pigment papers and their bromides. Several types of apparatus are available for combining the bromides and pigment paper with ease and consistency. After the bromides and pigments have been in contact for approximately ten minutes, the bromides are separated from the pigment papers and placed aside for redevelopment. Each pigment is then squeegeed, after being soaked briefly in cold water, to one of the waxed celluloids. All air bells must be removed and intimate contact between the pigment and waxed surface obtained.

Carbro pigments are somewhat affected by the temperature of the surroundings during sensitizing and bleaching operations. Modern gelatin pigments are less susceptible than the older types but precautions should be taken to keep the pigment papers between 18 and 20° C. Higher temperatures lead to veiled highlights.

Hot Water Development.—After approximately ten minutes, the celluloids may be placed in trays of hot water (50° C.) with the pigment paper uppermost. When the pigment commences to ooze out from the edges, this is the signal for the backing paper to be stripped away very carefully from the celluloid, during which operation the celluloid must be kept under the water. The pigment backing paper is discarded and development of the celluloids is continued until no more pigmented gelatin can be removed. Each celluloid is then given a brief rinse in cold water and set aside to dry.

Transfer to Soluble Support.—A piece of soluble support paper (coated with gelatin soluble at about 45° C.) is expanded in water for about ten minutes and when the cyan image is dry, it is also soaked for several minutes in water at room temperature. The two are then removed from the water, image in contact with the gelatin surface of the paper and squeegeed firmly together. When dry, the paper will leave the celluloid and carry the cyan image with it. The wax on the surface of the cyan image must now be removed with successive swabbings of turpentine, and polished dry. The soluble support bearing the cyan image is then resoaked in cold water with the magenta bearing celluloid and the two removed together and lightly squeegeed into contact. The magenta and cyan images must then be carefully registered, bending the sandwich if necessary, and then squeegeed firmly in contact before drying. A similar operation is carried out for the yellow image.

Transfer to Final Paper.—A piece of single transfer paper, rather larger than the temporary support, is soaked for ten minutes in hot water and then placed in contact with the soluble support bearing the three images from which the wax has been removed. This operation is carried out in a tray of water at room temperature. The two are withdrawn, squeegeed firmly together and placed aside between blotters under pressure to dry for thirty minutes. The sandwich of soluble and final support papers is then placed in a tray of hot water at 50° C. for about three minutes when the soluble support may be stripped away. The final support bearing the three images is washed with hot water until all the soluble gelatin is removed. The final color print is then briefly rinsed in cold water and taped to a glass plate to dry.

Dyebro Process.—The dyebro process is a hybrid making use of the carbro method of making a set of gelatin reliefs, and then using the relief imbibition method of dye transfer to form the final print on paper. In practice, a set of bromide prints is made from the color separation negatives using the same procedure as for the carbro process. The pigment papers for Dyebro come with a very slight pigmentation, just enough to make the image visible after transfer to the celluloids. These pigment papers are sensitized in the normal manner and contacted with the bromide prints. After bleaching is complete, the pigments are squeegeed onto plain celluloids and then developed in hot water in the usual manner. The absence of any wax coating on the celluloids enables the gelatin relief image to adhere firmly to the celluloid. When fully developed, the three celluloids bearing their relief images are briefly hardened in a formalin solution before drying. When dry, the films are dyed in a manner similar to that employed for imbibition matrix material. The dye images may then be transferred to a prepared gelatin surface in the usual manner.

Etching Processes.—A dye absorbing gelatin relief positive image may be made by chemically etching a silver negative. This process makes use of nascent oxygen from the etching solution to attack the colloid surrounding the finely divided silver grains. R. E. Liesegang observed in 1897 that the gelatin surrounding a silver image was softened and could be removed with hot water after the film was treated with a solution containing ammonium persulfate. This method was improved by M. Andresen[8] who used hydrogen peroxide with a halogen acid, and by Wall.[9] This process necessitates the use of a negative image to obtain a positive relief. Defender Pan Chroma Relief Film employs this procedure in obtaining positive relief images directly from positive color transparencies. Three films, dyed black in manufacture to restrict the penetration of the exposing light, are exposed from the emulsion side through tricolor analysis filters. After development to negative silver images, fixation and drying, they are treated with the cool etching bath. The reaction removes the negative silver image and adjoining gelatin leaving a positive gelatin relief. After fixation, washing and drying, the three films are ready for dying. Transfer of the dye images is carried out in the usual manner.

Differential Hardening of Dichromated Colloids.—The dichromate-colloid reaction may be used in several other ways to form a useful image. In contrast to the previously considered relief processes, use may be made of the hardening action of light or silver on a dichromated colloid to form images in which the distinguishing characteristic is the hardening or tanning to which various parts of the colloid have been subjected. A slight relief image may be formed in some of these processes but its presence is incidental and none of the colloid is removed. It may then be said that these processes are distinguished by the differential hardening of certain colloids, generally gelatin. All such processes become practical when it is noted that certain water soluble dyes and greasy inks react differently to hard and soft gelatin. For purposes of classification, it is possible to distinguish between those processes employing dyes and those using inks as the coloring medium.

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[8] *Phot. Korr.* (1899) 260.

[9] Wall, *Hist. of Three-Color Phot.* p. 356.

1. *Dye processes employing the differential hardening of colloids are generally, although not always, of the imbibition type.* Edwards in 1875 and Cros in 1880 discovered that a gelatin layer could be made to absorb some water soluble dyes differentially by properly hardening parts of the gelatin. This idea was further developed by Didier and sold commercially as the Pinatype processes. The dyes used in the Pinatype process were capable of staining soft gelatin in preference to tanned or hardened gelatin. If a gelatin layer contained an image of hardened gelatin, the dye would be absorbed by the reverse image—that is, by the soft gelatin. Thus, if the printing plate image was made from a negative, a negative dye image was created. The original process made use of the standard color separation negatives from which three positive transparencies were made. These transparencies were then used to expose the three sensitized colloids. The colloids, usually gelatin, were treated with dichromate and dried before their exposure to a strongly actinic light. The exposure hardened the gelatin in proportion to the transparency of the positive, thus giving a negative image of hardened gelatin. If such a plate is immersed in a Pinatype dye, a positive dye image is obtained. The film might be used either as a transparency or the dye could be transferred to a final support of soft gelatin as in the relief imbibition processes. It must be borne in mind that the printing plates made by this procedure are smooth and contain all the original gelatin, various parts of which absorb certain dyestuffs. As discussed under relief processes, there are many ways of obtaining an image of hardened gelatin and these other methods could be used as satisfactorily as the one described.

The practicability of such procedures is based on the selective action of certain dyes. Some dyes are known that exert their selective staining on hard gelatin in preference to soft gelatin and a color process may be based on such dyes. The application of processes of the above types are of course dependent on the existence of dyes fulfilling the differential staining requirements as well as the other prerequisites for subtractive color printing media.

2. *A second type of process employing a differentially hardened colloid is based on a somewhat different property of the colloid.* If a layer of gelatin containing hardened and soft portions is placed in a

water bath, the water will be freely absorbed by the soft gelatin and not by the hardened gelatin. If such a film is then inked with a greasy ink, the hard gelatin surface will adsorb the ink while the water soaked soft gelatin will reject the greasy ink. Such an ink image may be transferred to any paper surface. The photo-gelatin processes such as Collotype and Bromoil make use of such a procedure and are capable of the highest quality reproductions of mediums employing inks as a coloring material. In this process again, the method of obtaining the differential hardening of the colloid is not limited.

Dye Coupling or Color Development.—Dye Coupling processes are undoubtedly one of the most logical methods of obtaining color prints. Aside from the three separate films required, the procedure is exactly the same as that employed for normal black and white production. Color development involves the conversion of a latent image to metallic silver and the deposition at the same time of a coloring dyestuff. As the production of the dye is directly connected with the reduction to metallic silver, the dye alone will give a positive image proportional to the intensities of the exposing light. By the proper choice of developers, a set may be found producing the necessary subtractive colors—magenta, cyan and yellow. If three such films are prepared from a set of color separation negatives and if, after removing the silver image, they are superimposed, a color print results. Color development processes for paper prints have not as yet achieved any widespread commercial success.[10] There are several difficulties such as instability to light, poor spectral hues of the colors available and stained highlights. The future will undoubtedly see a growing field for color development processes. For the present, the greatest use of dye coupling development lies in the integral tripack processes discussed in Chapter XXXIII.

Dye Destruction Processes.—The Dye Destruction Processes date back to the early years of this century and are based on the chemical destruction of dyes in an emulsion containing a silver image. The emulsion is dyed fully and after the silver image is developed, the film may be treated with solutions which destroy either the dye in contact with the silver image or the dye in contact with the remaining silver halide. In either case, the color remaining after the removal of the silver and halides is a pure dye image in gelatin. Of the two methods of dye destruction or bleaching, the first is the more useful being the basis for the successful commercial processes. Since the

[10] Wilson, *Amer. Phot.* 33 (1939) 161. Friedman, *Amer. Phot.* 34 (1940) 851.

only present commercial use of dye destruction processes is in connection with integral tripacks, this process will be discussed in Chapter XXXIII.

Dye Bleaching.—In a photo-chemical system the only effective radiation is that absorbed by the medium itself (Grotthus-Draper Law). Most dyes fade when exposed to visible or ultra-violet radiation and many are known that fade so rapidly as to be useless for commercial purposes. Since any coloring agent transmits its own color and absorbs the remainder of the visible spectrum (its complementary color), a magenta dye, for example, is most effective in the absorption of green light, a red dye in the absorption of blue-green light, etc. Now if, for example, a layer of gelatin containing a suitable yellow dye is exposed to a colored positive, the dye will be bleached wherever blue light reaches the layer of gelatin. The blue radiation will be absorbed by the yellow dye and produce a photo-chemical change which results in the bleaching of the dye, while red and green will be transmitted freely and therefore not cause any appreciable alteration of the dye. Consequently, if three such layers, dyed with light-sensitive subtractive printing colors, are exposed to a positive image in color, a positive color picture will be obtained directly.

Such an apparently simple solution to the problem of obtaining color pictures has naturally been extensively investigated. At least two such processes have been exploited commercially; Utocolor paper produced by Smith in 1912 was an early commercial process [11] and Vitachrome paper has been recently introduced. There are a number of serious obstacles to be overcome in successful bleach-out processes, among them being the difficulty of obtaining sufficient sensitivity to permit reasonably short exposures, and a permanent absence of light sensitivity after the print has been made. It has also been very hard to obtain clean whites by means of the bleach-out process. In contrast to the success achieved to date, a very great amount of effort has gone into the development of bleach-out processes. The obvious simplicity of the system attracts so strongly that developments are still being made and future improvements may reasonably be expected.

Since most usable dyes are so slowly bleached by light as to be useless for practical work, various sensitizers or accelerators have been added to the different dyes to increase their light sensitivity.[12] The sensitizer may take the form of the dye carrying material (collodion or gelatin) or be present as added ingredients (other dyes, thiourea derivatives or oxides and salts of various metals with acids).[13] A study of the reactions of the various light-sensitive dyes has indicated both photo-chemical oxidation and photo-chemical reduction as taking place when the dyes are bleached, the exact reaction depending on the dye. A somewhat analogous method employs as the sensitive system dyes or leuco derivatives which will react as dyestuff generators when exposed to light.[14] In all these processes, the sensitizers are destroyed or removed by chemical treatment or by washing after the light reaction is completed. The final dye images are thus left relatively insensitive to light after the accelerating agents are removed.

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[11] *Phot. J.* **50** (1910) 141.

[12] *Amer. Phot.* **32** (1938) 821.

[13] *Brit. J. Phot.* **87** (1939) 455.
[14] *Brit. J. Phot.* **88** (1940) 624.

CHAPTER XXXII

SCREEN AND LENTICULAR PROCESSES

Introduction.—The Screen and Lenticular Processes are similar since they both contain in a single layer of emulsion the three color separation images. The three color records, as silver images, are physically separated laterally instead of vertically as in the integral tripack processes considered in the next chapter. In general, the colors observed are obtained by an additive synthesis.

The Screen Plate process was originally suggested by du Hauron in 1868 and has slowly developed since its first commercial use by Joly in 1894 to the present Dufaycolor screen film. The Lenticular process on the other hand is a relatively recent addition to the list of color processes, as the earliest mention of such a method was in 1908. The Lenticular method enjoyed a meteoric rise to prominence and, during the 1920 to 1930 period, it was probably the most widely investigated color process. Since the introduction of integral tripacks, interest has waned but there are developments still being made on new adaptations of the basic principles.

Screen Plate Processes

The screen plate processes are compartively simple to work and until recently were virtually the only processes of natural color photography practical for the average amateur or professional photographer. The greatest disadvantage of the screen plate processes is that they are incapable of producing prints on paper except by the rather lengthy and laborious process of making three-color separation negatives from the transparency and prints from these negatives by one of the subtractive printing processes. Another disadvantage is the limited range of brightnesses over which the screen plate processes are able to reproduce color satisfactorily, thereby placing a restriction on the subject matter suitable for reproduction. While more marked in some processes than others, this limitation is a necessary consequence of the medium-grain, thinly coated emulsion used to obtain sufficient resolving power to define sharply the fine color elements of the screen. The pattern formed by the screen is an objection in many cases, as when the image is to be enlarged or when critical definition is required. Lastly, the screens involve a great loss of light so that the image is dark unless a powerful source of light is used for illuminating the transparency or for projection.

Screen plates may be divided into two main classes: (1) separable and (2) inseparable screen processes. The separable screen is generally geometric in character and coated on a separate plate from the emulsion. The chief advantage of the separable screen lies in the possibility of producing duplicates simply and at low cost. The inseparable processes have their screen and emulsion coated onto a single support. The screen may be either of the geometric regular type or an irregular mosaic. Each of the above types has achieved commercial success.

The Requirements of a Screen Plate.—The following factors determine the performance of a screen plate:[1]

1. *The size of the color elements.* These must be below the resolution of the eye (visual angle of one minute, corresponding to 0.02 mm. at the average distance) but above the resolution of the emulsion. If too large, the elements are perceived individually; if too small, the color rendering cannot be true, since the emulsion is unable to record accurately the result produced by the screen.

For geometric screens, the color elements should not be larger than 1/300 of an inch or much smaller than 1/600 of an inch; for mosaic screens, the size should not exceed 1/900 of an inch or be less than 1/2000.

The color elements may be larger in a geometrical screen than in a mosaic because in the latter it is virtually impossible to avoid a certain amount of clumping on the part of color elements of the same color, thus giving rise to areas producing a dominant color.

2. *The transmissions of the color elements.* The requirements of the three-color taking filters have been discussed previously (p. 745). The transmissions of three-color viewing filters, unlike the taking filters, should not overlap and should be relatively narrow so as to produce brilliant, sharply defined colors (F. E. Ives). In a separate screen process, the transmission of the filters of the taking and viewing screens need not be the same, although, of course, the color elements must be of the same size in both screens and must conform to the same pattern. In a combined screen plate process, such Dufaycolor, Autochrom, etc., the same screen must serve both for taking and for viewing; the transmission of the color elements must represent the best compromise pos-

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[1] Mees, *J. Chem. Ed.* **5** (1928) 1578.

sible under the circumstances.[2] The average transmission of the screen elements for most of the present screen processes is as follows:

	Transmission Range	*Maximum Transmission*
Red Element	570–690 mμ	615 mμ
Green Element	480–620 mμ	535 mμ
Blue Element	400–530 mμ	470 mμ

3. *The relative area covered by each color.* This must be adjusted so that the screen appears neutral.

If the screen, as a whole, possesses a dominant tint, obviously it cannot reproduce colors correctly and a distortion of the colors of the original will result in the direction of the dominant color of the screen.

4. *The interstices.* These, if they exist, must be filled to prevent irradiation, which would greatly reduce the ability of the emulsion to image the color elements sharply and lead to color dilution.

5. *Thickness of the screen.* The screen must be as thin as possible to prevent parallax. The thickness should not in any case exceed the smallest dimension of the color elements.

6. *The emulsion.* This must be panchromatic, highly and as evenly sensitive as possible. If the emulsion is not equally sensitive to the light transmitted by the three filters of the screen, a color filter must be used over the lens in order that equality of action may be secured through all three filters. Its resolution must be equal to the color elements of the screen, and it must be able to produce a relatively high density in order that, where necessary, the color elements which should not function in the formation of an additive color can be stopped out. In the case of a screen plate in which the screen and the emulsion are inseparable, the emulsion must be adaptable to the requirements of the reversal process.[3]

Construction of Color Screens.—The irregular mosaic screens are made from a mixture of small colored particles. The particles may be of colored glass, powdered enamels, gelatin, resins, starch, flours, corpuscles or various gums. A mixture of appropriate amounts of the three colored particles may be obtained mechanically by sifting or by the use of ultra-sonic vibrations. Certain types of particles are emulsified in various media or atomized and allowed to settle onto a properly prepared plate. Whatever method is employed, the particles colored red, green and blue-violet are mixed so that the finished screen is nearly neutral. If the screen particles do not completely cover the plate, an opaque material such as carbon or dye must be employed to fill the interstices.

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[2] Mees, *Brit. J. Phot.* **55** (1908) 41; **58** (1911) 45, 52, 62, 68, (col. suppl.).

[3] Thorne-Baker, *Phot. J.* **72** (1932) 109.

The geometrical screens, whether of the separable or inseparable type, are generally produced either photographically or mechanically. The basis of both types was laid by du Hauron in 1897 and Joly in 1894. The photographic procedure employs most of the methods used in the production of color prints, such as the dichromate-light or silver hardening reactions, the differential staining by certain types of dye, as well as chemical toning and dye coupling. In the mechanical methods, the film base or an over-coat is dyed and then ruled with a greasy protective resist. The unprotected film is bleached, re-dyed another color, and the resist lines removed. This procedure is repeated for the third color.

Over the completed screen, whatever its nature, a protective layer is placed before the panchromatic emulsion is coated. This layer must be thin to avoid parallax, waterproof to prevent the processing solutions from affecting the screen, and adhesive enough to hold the emulsion firmly and also adhere to the screen layer below.[4]

The Lumière Filmcolor.—The first commercially successful screen plate was the Lumière Autochrom introduced commercially in 1907. This plate was of the inseparable screen type.

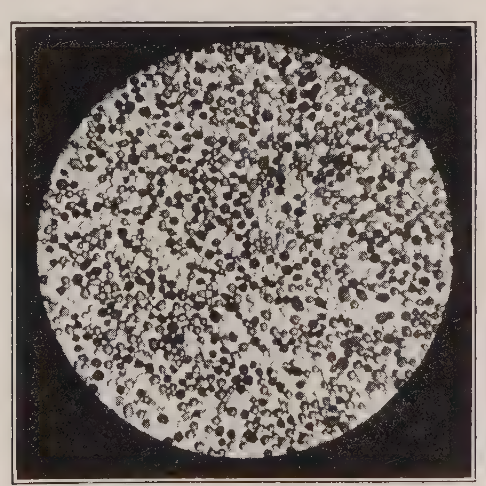

FIG. 371. Photomicrograph of the Autochrome Screen.

[4] *Brit. J. Phot.* **85** (1938) 805.

The screen (Fig. 371) is composed of grains of potato starch about 15/1000 millimeter (.0024 inch) in diameter, colored orange, green and blue-violet. The grains of potato starch are first passed through a sieve to obtain a uniform grain size and then divided into three groups, each of which is dyed. The grains are then mixed thoroughly (in the ratio of 4 green to 3 red and 2 blue) to secure even distribution of the different colored grains and then dusted on film base which has been coated previously with a suitable substratum. The interstices are filled in with a fine opaque powder and the layer smoothed out by rolling under heavy pressure. The screen is next covered with a thin layer of waterproof varnish over which is coated a panchromatic emulsion. The screen is not white but a light salmon pink and transmits approximately 7.5% of the incident light.[5]

In 1932, the Autochrom screen was supplied on film under the trade name, Filmcolor. The original Autochrom plates on glass have since been discontinued.

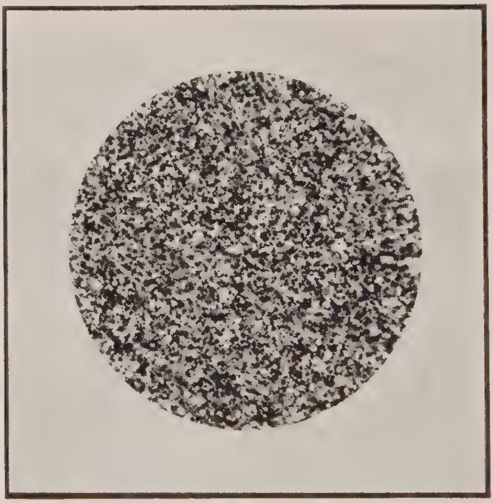

FIG. 372. The Agfacolor Screen.

Agfa Ultracolor Plate.—This mosaic screen, recently discontinued, was made from dyed particles of gum arabic rolled out in collodion (Fig. 372). The size of the color elements was about the same in the Agfacolor screen as in the Autochrom but was more uniform, varying from 0.008 to 0.017 millimeter.[6] The screen, however, transmitted nearly twice as much light as the Autochrom because of the slightly higher transparency of the colored grains and the lack of black material between the grains. The color elements completely covered the plate in the Agfacolor screen, no filler being required. The relative transmissions of the Agfacolor and Autochrom screens are 14 and 7.5% respectively. This material was also available coated on film base.

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[5] Ventujol, *Amer. Phot.* **18** (1924) 384.

Dufaycolor.—This process, unlike the two previously discussed, employs a geometrical type screen or reseau (Fig. 373).

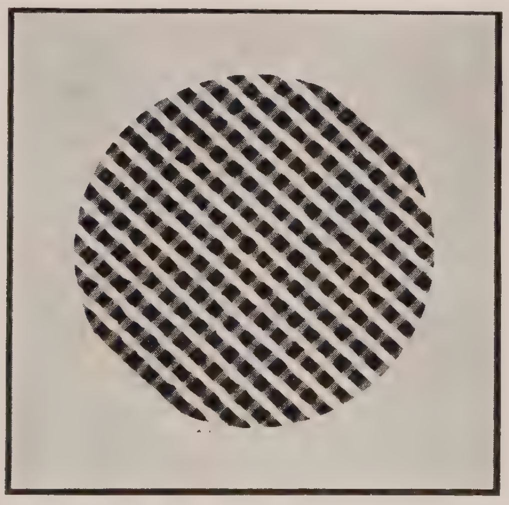

Fig. 373. The Dufaycolor Screen.

The acetate film base is first coated with a very thin layer of collodion, dyed blue; this step is followed by printing a set of greasy ink lines with engraved rollers at an angle to the length of the roll, there being twenty lines to the millimeter and the interspaces being equal in width to the lines. In the next operation, the dye between the ink lines is bleached and a green dye colors these clear spaces. The ink is dissolved and a series of blue and green parallel lines remains, covering the entire film base.

A second set of ink lines is now printed at right angles to the first. The lines this time are broader than in the first instance and the spacing narrower, but there are the same number per millimeter as before. The second bleaching bath removes the green and blue dye where there is no protecting ink and the spaces are dyed red. The ink resist is removed, resulting in a microscopic regular pattern of green and blue squares, with red lines in absolute juxtaposition. The reason for having the red lines narrower is to approximately equalize the areas of red, green and blue. A protective varnish is coated over the screen to prevent desensitization of the highly panchromatized emulsion used. Dufaycolor film is supplied in both cut sheet and roll form. These normal emulsion types are slightly different as to speed and color balance so that one material will be closely adapted for the lighting conditions employed, without the use of heavily correcting color filters. Special emulsions, medium and hard, are also available when higher contrasts are desirable.[7] Because of the lack of contrast control in normal reversal processing, these special contrasts are advisable for the best reproduction of copy material, such as paintings or maps.

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[6] Pledge, *Brit. J. Phot.* 70 (1923) 48 (col. suppl.).

Exposure of Screen Materials.—Color screen materials are exposed in the camera with the emulsion side away from the lens so that the incident exposing light will pass through the color screen before affecting the sensitive emulsion. If the screen support is glass, a focusing adjustment must be made to compensate for the lengthened light path. Screen materials range in speed from that of a medium speed black and white material (Weston 8) down to one of one-twelfth of that value. The color sensitivity of the panchromatic emulsion and the screen-transmissions determine the color temperature of the light source for which the material is balanced. Compensating filters are generally supplied for altering the quality of the light reaching the emulsion. If, for example, the chosen emulsion is for use in daylight, compensating filters may be used for all types of artificial light. Some processes supply two different screen emulsions, one balanced for daylight, the other for a chosen incandescent lamp. The maximum speeds are obtained by this method since very weak or no compensating filters are required under normal conditions.

The inseparable screen processes are generally used as positive transparencies and are, therefore, processed by reversal. The limitations of all normal color processes as to the short brightness range that can be satisfactorily reproduced are emphasized by the reversal process. For satisfactory viewing and speed in exposure, the coating weight of the emulsion must be kept low. This factor leads to a very limited latitude. For this reason alone, it is advisable to compress the brightness range of most subjects if an accurate color reproduction is desired, on the color transparency, of various parts of the subject.[8]

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[7] Beale, *Phot. J.* **81** (1941) 108.

Processing of Inseparable Screen Materials.—Inseparable screen materials processed by reversal avoid registration difficulties since the originally exposed film becomes the final color positive. Special processing methods and emulsions have been developed for the reversal procedure, and the generally accepted method for color screen materials has been the employment of developers containing silver halide solvents.[9] In normal reversal processing, such substances as the thiocyanates and ammonia, included in the first developer, lead to clear highlights and an effective increase in speed. Similar solvents are also used in the negative-positive processing of screen materials but for a somewhat different purpose.

The color screen material is first developed in a developer of high activity containing the halide solvent. The following Dufaycolor first developer is a typical example:

	Metric	*Avoirdupois*
Metol	1 gm.	16 gr.
Sodium Sulfite	50 gm.	1¾ oz.
Hydroquinone	8 gm.	128 gr.
Sodium Carbonate	35 gm.	1¼ oz.
Potassium Bromide	5 gm.	80 gr.
Potassium Thiocyanate (Sulfocyanate)	9 gm.	144 gr.
Water to make	1000 cc.	32 oz.

Screen material may be developed either by time and temperature or by inspection. If the exposure is correct, the former method is suitable, but for unusual subjects or unknown conditions, inspection is preferable. A visual check along with a time-temperature schedule is undoubtedly the safest procedure. The material may be desensitized in Phenosafranine if desired, and processing carried out in a fairly bright light.

After development, the film is washed in running water for one minute or a dilute acid stop bath may be used. The silver image is next bleached in an acid solution of bichromate or permanganate until all the black silver has been removed. The last stages of this operation and all the following steps may be carried out in bright light. When bleaching is complete, the film is washed briefly before clearing in an aqueous solution of sodium bisulfite. The film must then be washed and exposed fully before development. The second developer may be the same one that was used during the first development or a separate bath may be used. A suitable formula is:

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[8] Yule, *Brit. J. Phot.* **87** (1940) 578.

[9] Turner, *Brit. J. Phot.* **84** (1937) 435.

Sodium sulfite	75 gm.	2 oz. 220 gr.
Amidol	15 gm.	220 gr.
Water to	1 liter	32 oz.

Development is carried to completion. The conversion of the positive halide image may also be carried out without re-exposure by chemical reducers such as sodium hydrosulfite or fogging agents. In any case, it is desirable to immerse the color transparency in a hardening fixing bath after the positive image is obtained. A thorough washing completes the processing. Contrast films, such as Dufaycolor Hard, are developed in a somewhat more contrasty developer than the normal emulsions, but the rest of the procedure is identical.

The color transparencies may be treated with the usual reducers and intensifiers if correction is desired. The reduction is carried out with Farmer's Reducer, while the silver or mercury intensifiers seem most suitable. Corrective work should be done with caution and in moderation.

Separable Screen Processes.—The only separable screen process receiving widespread use in the past has been the Finlay Process. This process, unlike those already discussed, is a separate screen process;

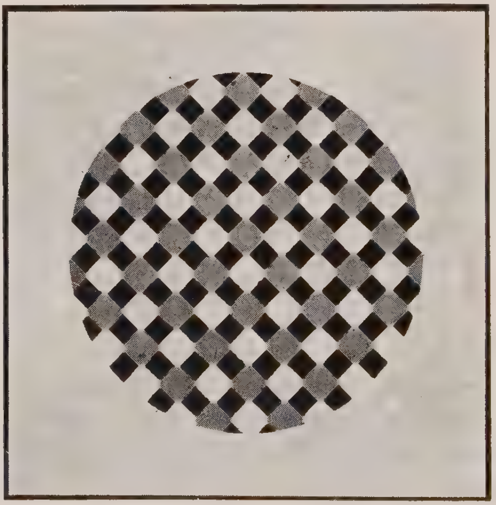

Fig. 374. The Finlay Screen.

that is to say, the screen and the emulsion are on separate glass plates which are placed in contact in a suitable holder for the exposure.

The screen (Fig. 374) is composed of red, green and blue color elements approximately $\frac{1}{300}$ of an inch square. It is made by printing in dyed bichromated albumen from a black and white cross-lined screen.[10] The glass plate is first coated with collodion containing a tricolor green dye. It is then coated with bichromated albumen and exposed beneath the cross-ruled screen. The areas not protected by the insoluble albumen are bleached out and dyed with a tricolor red dye. The plate is coated with albumen a second time and exposed between a cross-lined screen so as to render the bichromated albumen insoluble over the red color areas, the unprotected areas bleached and dyed with a tricolor blue dye. A final protective layer of collodion is coated over the finished screen.

As the screen and the sensitive material are separate, a special plate holder with a pressure back must be used to insure perfect contact between the screen and the sensitive emulsion. The taking screens may be used over and over if care is taken to avoid marking the surface. A standard panchromatic emulsion is employed and compensating filters placed over the camera lens allow operation under several qualities of illumination.

The panchromatic emulsion is developed in a soft negative developer and printed by contact onto a slow contrast emulsion. This positive transparency should be bright and clear and of a medium density. When dry, the positive is bound in register with a viewing screen. The color elements of this viewing screen are of the same size and orientation as in the taking screen, but of slightly different transmissions to obtain the most desirable color reproduction. The possibility of using different taking and viewing filters allows slightly higher color accuracy to be obtained with the separable screen processes. Unlimited duplication of the black and white positive allows any number of color transparencies to be made simply and at low cost.

Copying Screen Materials.—The duplication of a separable screen color transparency simply involves the production of another black and white positive to be registered with a viewing screen. The inseparable screen transparency, on the other hand, is difficult to duplicate satisfactorily. The distribution of energy from the color transparency is not the same as that from the original scene, although the visual sensation may be similar. The simple procedure of contact printing gives very degraded colors, due to the addition of black in the picture as shown in Fig. 375. Since the elements of the two screens will not exactly line up under normal conditions, the light from any given color element of the original may not fall on the same color elements of the screen in the new film.[11] The close combination of two geometrical screens will also cause difficulty with moiré pattern.

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[10] Stobart, *Phot. J.* **76** (1936) 280.

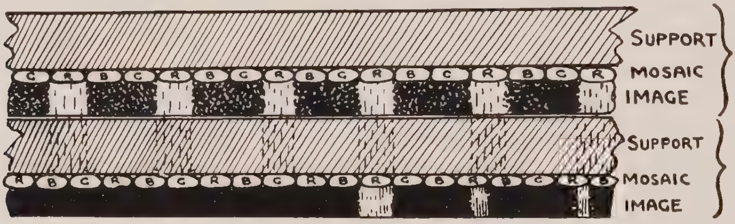

Fig. 375. Increase in Proportion of Black When Copying by Parallel Light. (Spencer, Photographic Journal. 1933.)

Another serious error is introduced by the scatter of the exposing light in the second emulsion. The emulsion below the screen elements surrounding the color element through which the light is passing should not be exposed, but by irradiation it is exposed slightly leading to a loss in density at those points after reversal. As the surrounding elements are of the other two primary colors, the final transmitted light will be desaturated by the addition of white[12] (Fig. 376).

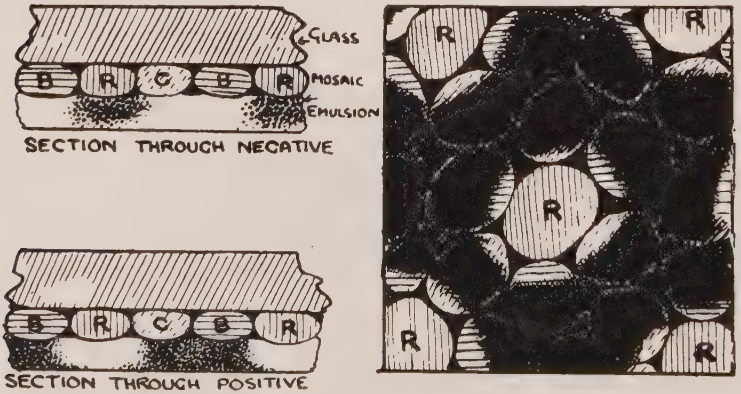

Fig. 376. Loss of Saturation Through Irradiation in the Emulsion. (Courtesy of Spencer, *Photographic Journal.*)

[11] Mees, *Brit. J. Phot.* **54** (1907) 49 (col. suppl.).

[12] Spencer, *Phot. J.* **73** (1933) 19.

The first two difficulties may be overcome by the complete diffusion of the light from the color screen of the original transparency before it strikes the screen of the film to be exposed. The necessary light spread may be obtained by separating the two films by the proper space if contact printed,[13] or if printed by projection, by making use of the diffraction effect or throwing the screen slightly out of focus.[14] Such procedures emphasize the third difficulty, that of irradiation in the color film emulsion. A fourth difficulty giving rise to a similar dilution of the colors is caused by the overlapping transmissions of the three color elements making up the color screen. Thus, if light from the original transparency comes from the red screen elements, it will not only expose the emulsion behind the red elements of the copy film screen, but will also partially affect the emulsion behind the green elements of the screen. A similar effect occurs with each color. This type of color dilution may be overcome by making use of three monochromatic or narrow color bands instead of white light for exposure when copying. Each of the wave length regions chosen must be wholly within the transmission band of only one of the screen elements.

Negative-Positive Processing of Inseparable Screen Material.—The logical method to employ for making a series of colored copies is to develop the original screen film to a negative and to make a number of identical positives by contact or optical printing. The same difficulties with moiré and color dilution due to the overlapping screen transmissions are encountered. Poor copies are obtained, however, even when corrective measures are applied. Harrison and Spencer found that a "color contrast effect" present in reversal processing was absent in normal negatives upon processing and made the color dilution due to irradiation in the emulsion a serious factor.[15] The color contrast effect, obtained with developers containing silver halide solvents, is neutralized in reversal processing by the light spreading due to irradiation. With development to a negative, the light spreading was not neutralized and serious color dilution resulted. The irradiation can be kept to a minimum by using depth developers which remove the surface halide

[13] von Huebl, *Brit. J. Phot.* **57** (1910) 59. Harrison and Horner, *Phot. J.* **79** (1939) 320.

[14] Tritton, *Brit. J. Phot.* **84** (1937) 513.

[15] Harrison and Spencer, *Phot. J.* **77** (1937) 250.

FARMER—Brit. J. Phot. **56** (1909) 3, 71, (col. suppl.).
HARRISON AND HORNER—Phot. J. **79** (1939) 320.
BAKER—J. Soc. Mot. Pict. Eng. **31** (1938) 240.

and keep the developed image lying close to the color screen.[16] The depth developers generally contain sodium thiosulfate although other compounds have been suggested. A typical formula is:

Metol	2.5 gm.	36.5 gr.
Sodium Sulfite	12.5 gm.	183 gr.
Hydroquinone	2.5 gm.	36.5 gr.
Morpholine ($NH(C_2H_4)O$)	10.0 gm.	146 gr.
Potassium Bromide	2.5 gm.	36.5 gr.
Sodium Thiosulfate	3.75 gm.	55 gr.
Water to	1 liter	32 oz.

Development to gamma of 0.85 in 4½ minutes at 68° F.

Color Separations from Screen Materials.—The color screen processes give three color records at a single exposure and, for color printing purposes, these records must be separated out onto three distinct emulsions. The separable screen process is the simplest and most effective in use since a black and white block-out screen is all that is needed to allow separation negatives to be made directly from the color transparency. The block-out screen allows but one set of color elements to be observed at a time for copying.

The inseparable screen processes are somewhat more difficult in that the same problems of screen removal, color dilution and overlapping transmissions that were considered in the last section must be taken into account. It is possible to make separation records from either a screen negative or a positive. The screen negative is preferable in that approximately double the latitude is present in such a film as compared to one processed by reversal. The majority of separation work with screen materials is done from reversal positives, however, since negatives are required for most of the color printing processes.

A long scale emulsion should be employed for separation since the average density range of screen transparencies is about 2.00. The transmissions of the color screen elements overlap considerably because of the necessity of short exposures for the screen film in the camera, and for a satisfactory luminosity when viewing the finished color transparency. Each of the color separations must record the densities lying behind only one of the screen colors and for that reason the separating filters must be very sharp cutting. In Fig. 377 it will be seen that each of the Dufay 1S, 2S and 3S transmissions falls within the region of one of the screen filter elements. Monochromatic lights may also be employed. The filter transmissions should be kept as narrow as possible in view of exposure requirements. Separation negatives should be kept to a fairly low gamma to hold the tones of the transparency on the straight line of the emulsion's characteristic curve.

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[16] Murray and Spencer, *Phot. J.* 77 (1937) 330, 458.

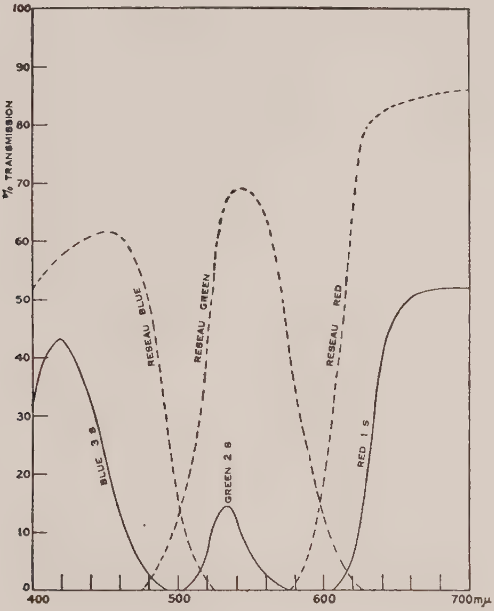

Fig. 377. Reseau and Analysis Separation Filter Transmission.

The Lenticular Process

The second basically additive method is the Lenticular process. This procedure was originally developed by Berthon (1909) and Keller-Dorian (1914) and reached its greatest application in this country when the Eastman Kodak Company in 1925 acquired the rights for its use and in 1928 presented 16 mm. motion picture Kodacolor. The appearance of integral tripacks has sharply curtailed developments in the Lenticular field but a few firms, mainly in Europe, are still experimenting on Lenticular improvements.

The Lenticular process is essentially a screen method in which the screen is formed optically on the emulsion during exposure. The film is colorless. Berthon proposed to place a banded three-color filter over the camera objective and, by means of small lenses or lenticules on the surface of the film base, to obtain small images of the objective and its

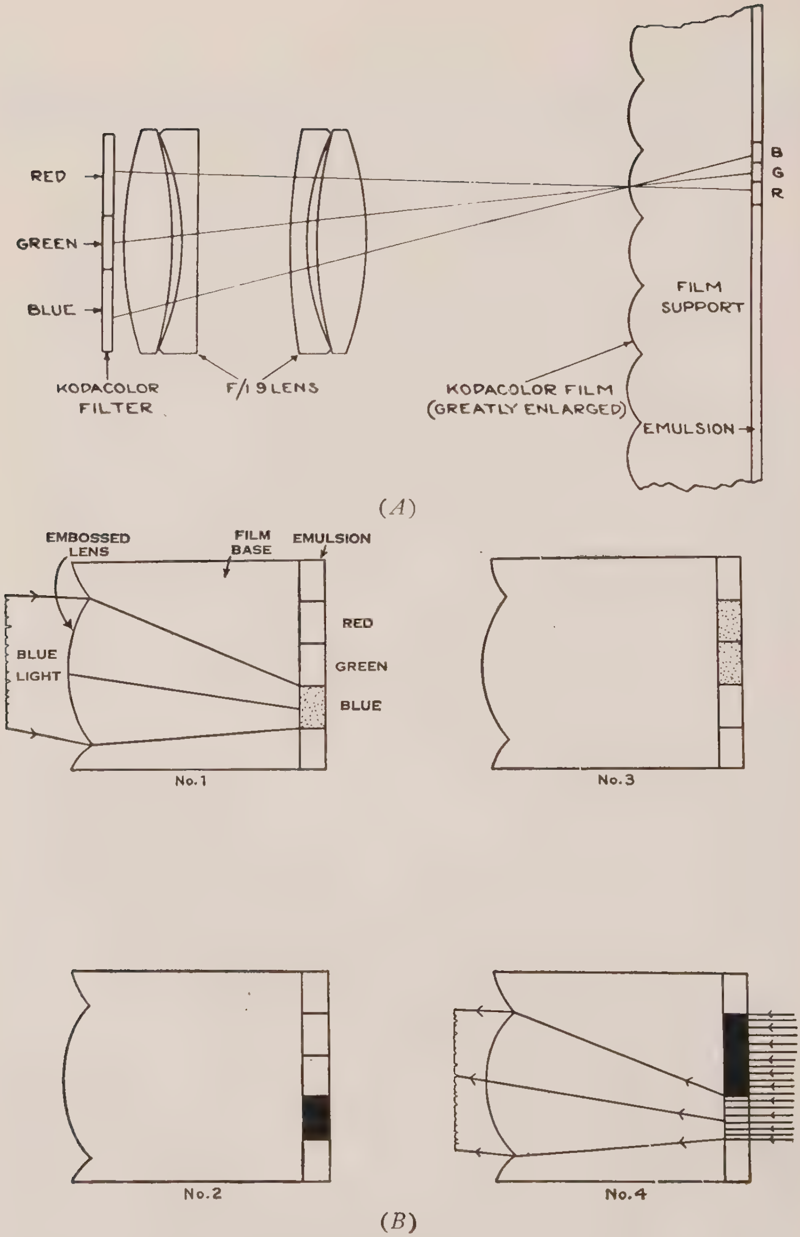

FIG. 378. General Optical System of Kodacolor Lenticular Process, (*A*). Enlarged Sections of Film (*B*) Show Image Formation in Four Stages: (1) Exposure, (2) Development, (3) Bleaching and Reexposure, and (4) Reversal Development and Final Projection.

filter on the emulsion of the film. Kodacolor film contained about 600 lenticules per inch (see Fig. 378). From a white card, for example, a series of three small colored images is projected onto the emulsion behind each lenticule, while a red card will be shown by only a single image since the red light will only be transmitted by the red section of the three-color filter. The original film is processed by reversal and projected back through a similar appropriate optical system of lens and filter. As normally projected the colors are obtained additively with the aid of the limited resolving power of the observer's eye.

The Lenticular process is theoretically a most elegant solution to the problem of color reproduction, but in practice so many, so far insurmountable, obstacles arise that the use of this method seems to be declining rather rapidly. Difficulties of diffusion, film shrinkage and eventual distortion, maintenance of color balance and limited depth of field are serious problems to be overcome. Other difficulties arise in copying, such as color wedging, moiré, and low color saturation, while in the motion picture field especially the necessity for special viewing (projection) apparatus has proven to be a serious obstacle to commercial acceptance. Because of these difficulties, the tendency in recent years has been to employ the Lenticular idea for the negative part of the color process only, or to use the Lenticular principle for a portion of a single color process which may later be printed subtractively.

The latest Lenticular method commercially available, called Pantachrome, has been devised by Agfa and involves the use of parts of a number of color processes.[17] The Lenticular phase of the process involves the making of two of the three color separation records, while the printing is all done subtractively. A Lenticular bipack is exposed in the camera, the front film being sensitive to blue and green, the rear emulsion to red. On the base of the front film, the usual Lenticular ribbing allows the formation of an image of the objective. The lens filter is composed of three bands. In daylight, the central band is magenta and the outside two bands are yellow (colors reversed for incandescent illumination). The front film records by the normal Lenticular method, the blue and green records as a line screen pattern, while

[17] *Phot.Tech.* **1** (1939) No. 7, 49.

Weil—J. Soc. Mot. Pict. Eng. **20** (1933) No. 4.
Capstaff, Wilder and Miller—J. Soc. Mot. Pict. Eng. **28** (1937) 123.
Guetener—J. Soc. Mot. Pict. Eng. **28** (1937) 447 No. 5.
Friedman—Amer. Phot. **34** (1940), 689, 754, 835.

the rear film records the red record in a continuous tone, since both filters transmit red light. The front film is developed by reversal and the rear film as a negative. The three-color separations are printed onto a single film, the cyan image being obtained from the back negative record by a standard iron toning method. The positive Lenticular records from the front emulsion are printed optically onto a double layer emulsion on the reverse side of the single film and the magenta and yellow positives obtained by the standard dye destruction procedure used in Gasparcolour.

CHAPTER XXXIII

INTEGRAL TRIPACKS

Introduction.—Three subtractive color processes of increasing importance are Dye Bleaching, Chemical Dye Destruction and Dye Coupling Development. These methods of color formation are, at the present time, intimately involved in the development of Tripacks. All three processes are commercially available in this form. Whenever more than one emulsion is coated on a single support, the term "integral" is generally applied. An integral tripack consists of a single support with three light-sensitive systems on one side. It may also be called a monopack. The three emulsions are not separable and must be handled together during processing. There are many other methods of employing the three light-sensitive systems such as, for example, a single support bearing two emulsions on one side and a third on the opposite side, or two emulsions coated on one support and the third on a second support. For purposes of classification [1] and discussion, various possibilities are listed in Fig. 379. The number of possible combinations which may be employed to obtain the three-color records is quite large but this chapter will be concerned chiefly with color formation by the three-color processes mentioned above when used with Integral or Two-sided Tripacks. The general term "integral tripack" will include all types unless otherwise mentioned.

Integral tripacks may be considered from two viewpoints: (1) the physical problems inherent in the coating of more than one emulsion on a single support, and (2) the chemical and photographic problems involved in the formation of usable colored images in the appropriate emulsion layers. The growth of integral tripacks has been closely allied with that of the three above-mentioned subtractive color processes, but it must be kept clearly in mind that the two are not synonymous. The development of integral tripacks has led to the commercialization of these processes but the tripack itself may be employed with other methods of color formation. It is likewise true that the dye bleaching,

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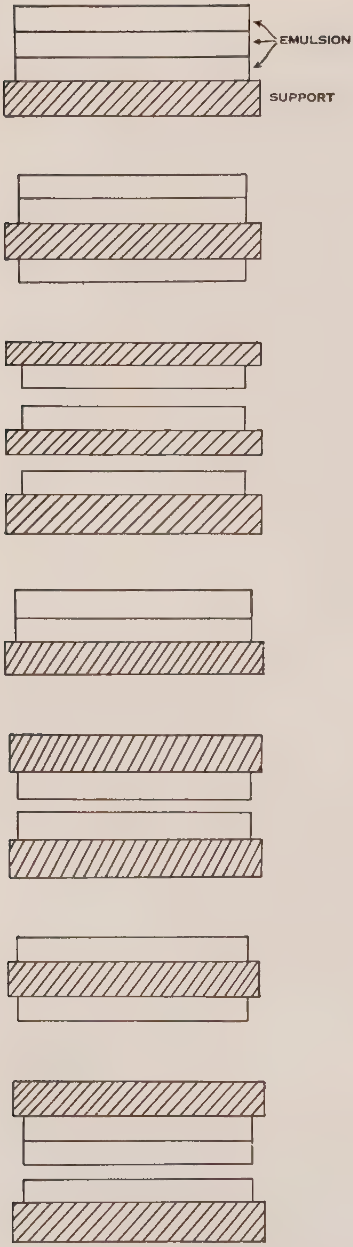
[1] Screen and lenticular processes may also be considered as tripacks where the three color records are separated laterally instead of vertically as in the integral tripack.



1. *Integral Tripack or Monopack.*
Three light sensitive emulsions coated on one side of a supporting base.

2. *Two Sided Integral Tripack.*
Two light sensitive emulsions coated on one side of a supporting base, the third on the reverse side.

3. *Separable Tripack.*
Three light sensitive emulsions on three separate supports—exposed in contact.

4. *Integral Bipack.*
Two light sensitive emulsions coated on one side of a supporting base.

5. *Separable Bipack.*
Two light sensitive emulsions coated onto two separate supports. Emulsions exposed in contact.

6. *Two Sided Bipack.*
Two light sensitive emulsions on opposite sides of a single support.

7. *Double Support Tripack.*
An integral or two sided bipack in contact with a single emulsion on a second support.

Fig. 379. Tripacks and Bipacks.

dye destruction and dye coupling reactions may be carried out in media other than the integral tripack.

Historical Development.—The idea of using a tripack to record a set of color separation images may be traced back, as is often the case with color processes, to du Hauron,[2] who in 1896 laid down the principles of the separable tripack and bipack. Selle,[3] in 1899, suggested the sensitization of a normal emulsion with a double dye bath of alcohol and water. One of the sensitizing dyes, soluble in water, penetrated to the lower depths of the emulsion and sensitized to green while the other dye, soluble in alcohol, red-sensitized the upper surface only, since it was unable to reach the interior of the emulsion. In this manner, a single zone-sensitized emulsion was obtained with the upper stratum capable of recording the red latent image, the lower level recording the green. Smith suggested, and produced in 1903, a coating of two or more emulsions, separated by intermediate collodion layers, onto a single support. The emulsions were subsequently stripped apart for processing. K. Schinzel[4] in 1905, and Sforza in 1909, proposed integral tripacks in which the sensitized emulsions were colored with dyes which were to compose the final image. This type of integral tripack was eventually developed into the present integral tripack dye destruction process, while Fischer employed dye coupling development in his monopack suggestions of 1914. This growth of multi-layered materials was paralleled by many other disclosures of bipack and tripack construction and usage, some of which are discussed in connection with the three subtractive processes to be considered.

Construction of Multi-layered Materials.—Many of the features of a multi-layered material are directly concerned with the method of

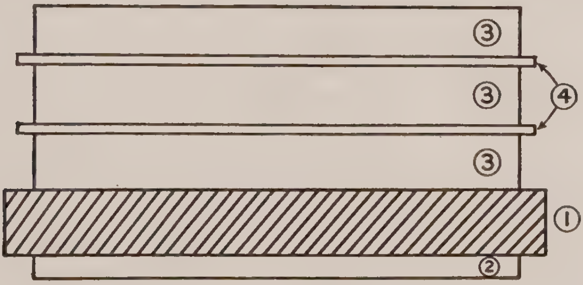


FIG. 380.

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[2] du Hauron, *La Triplice Photographique* (1897) 223.
[3] Selle, B.P. 12,516.
[4] Schinzel, *Phot. Woch.* (1905).

color formation to be employed, but the essential factors common to most such materials will be considered in this section. A typical integral tripack, shown in Fig. 380, consists of: (1) a film, paper or glass support; (2) an anti-halation coating; (3) three separate light-sensitive emulsions, usually separated from each other by (4) thin layers of gelatin. The rigid requirements for integral tripacks demand the utmost skill in emulsion manufacture and coating. Following are some of the characteristics of the elements in a typical monopack:

1. *Physical characteristics of the emulsions.* The thickness of the complete monopack is approximately 0.04 mm., so the individual coatings are extremely thin. The thickness varies rather widely, depending upon the subsequent usage to which the material is to be put—negative or reversal processing—and the type of color formation to be employed. The lowest emulsion next to the support varies from 0.015 to 0.02 mm., while the upper emulsion or emulsions are approximately 0.005 to 0.01 mm. in thickness. To allow adequate light transmission to, and to obtain sharp images in, the lower emulsion, the uppermost emulsions are sometimes poor in silver salts, having been diluted with clear gelatin to preserve their transparency. On the other hand, the halides must be present in sufficient quantity to allow the development of an adequate silver image, later to be converted to a color image. The emulsions may carry not only light-sensitive silver halides, but also sensitizing and light-filtering dyes and substances for the formation of the colored images besides. The production of stable, non-migrating sensitizing and filter dyes is one of the most important reasons for the commercial excellence of integral tripacks.

2. *Photographic characteristics of the emulsions.* The two or three light-sensitive coatings must be so arranged and sensitized that each records one of the desired spectral regions. The order of coating the various emulsions is not of fundamental importance although the red-sensitive layer is generally placed at the bottom of the pack. The color recorded by any particular emulsion is determined by its inherent sensitivity after sensitization, and the light-filtering action of other emulsion or dye filter layers above it. The speed and contrast of each of the emulsions should be so balanced that with some given form of illuminant and processing, the photographic tone reproduction will be correct in each layer. The sensitizing dyes in the various emulsions must not diffuse into adjoining layers and affect their sensitivity, and the particular halides (chloride, bromide, iodide) employed will be somewhat dependent on the method of color formation subsequently to be employed.

3. *Characteristics of the separating layers.* The intermediate layers between the light-sensitive emulsions serve one or more purposes, the most important of which are: (1) to act as color filters for the sensitive emulsions, and (2) to aid in the differential processing of the various emulsions after exposure. The layers may consist of gelatin or of some other substances depending on the purpose of the layer; for example, waterproof layers may be employed. If of gelatin, the layer is about .001 mm. thick and may or may not contain filter dyes or silver salts. The use of the various types of separating layer are discussed further in connection with the formation of colored images in the tripack.

Color Formation in Tripacks.—The real problems in connection with the use of integral tripack materials come with the conversion of the three latent or silver images into usable colored images. In some cases it may only be necessary to obtain a color negative for reseparation or printing, but at present the tripack methods are generally processed by reversal. The conversion of the silver images into color may be carried out by almost any of the subtractive printing methods, such as chemical or dye toning, or the dye bleach, destruction or coupling processes. The most important methods of color formation are the silver dye destruction and dye coupling development processes.

Silver Dye Destruction Processes.—These processes are based upon the chemical destruction of a dye present in the emulsion layer. The destruction of the dye may be made to take place either in the presence of a developed silver image or in areas without a silver image. In either case, the silver image is the agency that controls the position of the dye image remaining in the film after chemical treatment.

Schinzel,[5] in 1905, proposed to coat an integral tripack with three silver halide emulsions which were dyed colors complementary to their light sensitivity. After development and fixation, the pack was treated with a dilute solution of hydrogen peroxide which destroyed dye in the presence of the silver image. The removal of the silver image and "attacked" dyestuff left an inverse dye image in each layer. Christensen discovered that finely-divided silver (in the form of the silver image) acted as a catalyst in the destruction of certain types of dye. Dyes which were attacked either slightly or not at all in the absence of silver were readily attacked in the presence of silver. Christensen[6]

[5] Schinzel, *Brit. J. Phot.* **52** (1905) 608.

[6] Christensen, *Eder's Jahrbuch* **29** (1915) 164; *Brit. J. Phot.* **68** (1921) 96.

HEYMER—Sci. Pub. Agfa Central Lab. **4** (1935) 177.

also proposed to use the reducing agents themselves for attacking the dyes and suggested sodium hydrosulfite. In this way, the dye was destroyed as the silver image was developed. The same result was obtained by Luther and Holleben[7] who chemically converted the silver image into substances which directly or by treatment with another reagent destroyed the dye. They suggested vanadium ferricyanide and chromic acid among other reagents.

The Gaspar patents since 1930 are concerned with the coating and processing of tripacks in which the color formation is based on chemical dye destruction. The destruction of dye contained in an emulsion layer in areas not containing a silver image may be carried out by baths similar to the following:

Calcium Hypochlorite..............	10 gm.
Glacial Acetic Acid................	10 cc.
Water to make....................	1 liter

Immersion in this solution destroys the dyes wherever they are not protected by the silver image. The inverse process may be carried out by using baths which do *not* normally affect the dyes in the emulsion, but in the presence of silver are able to attack and bleach the dye. A typical dye destruction bleach bath is composed of

Potassium Thiocyanate............	30 gm.
Citric Acid........................	30 gm.
Water to make....................	1 liter

The reagents which may be used in the inverse process fall into several classes,[8] such as

1. Nitrogenous organic compounds
2. Compounds of thio urea
3. Special sulfur compounds
4. Certain acids indifferent to the dyes employed.

More recent applications[9] of the same principle have been concerned chiefly with: (1) the improvement of the above method, (2) the development of procedures for the formation of the dyes in the emulsion layers *AFTER* exposure rather than inclusion of the color in the emulsion when coated, and (3) the conversion of the silver image into other substances more useful in the subsequent dye destruction. A tripack composed of three emulsions dyed cyan, magenta and yellow is extremely slow and rather impractical for camera exposures. The employment of dye destruction reagents which destroy dyes in the presence of silver, also necessitates the use of positives for exposure since a positive image is required. The desirability of negative materials has recently been met by the employment of various dye generators.

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[7] D.R.P. 396,485.

[8] *Brit. J. Phot.* **27** (1933) 41 (col. suppl.).

[9] *Brit. J. Phot.* **86** (1939) 198; **87** (1940) 7, 419, 433, 459, 468; **88** (1941) 220, 292.

Dye Coupling Development.—The formation of a dye image in conjunction with the development of a silver image may take two forms, known as primary and secondary color development. In primary color development, the oxidation product of the development is a dye, while secondary color development involves the oxidation of the developing agent and its combination with another substance (coupler) to form the dye.

The growth of primary dye coupling development goes back to Homolka,[10] who, during the course of his investigations of the latent image, desired colored insoluble development products. Developing agents which gave colored images had been known—such as pyrogallol—but Homolka used indoxyl and thioindoxyl to obtain blue- and red-colored images of indigo and thioindigo along with the silver images. Homolka did not apply this discovery to color photography, and Fischer, in 1914, patented these primary color developers for the formation of monochrome prints. Fischer and Siegrist [11] laid down the foundations of secondary color development at the same time and showed how the oxidation product of developers such as paraphenylenediamine and para-amino-phenol could couple with phenols and amines to form dyes of the indophenol, indamine or indoanilin classes. The application of such procedures to multi-colored images was suggested at about the same time by the Neue Photographische Gesellschaft in connection with the formation of color photographs.

Primary color development is rather restricted in its application because of the rather limited range of colors which can be obtained. Primary color development [12] has been suggested for obtaining a yellow image of higher contrast during a normal secondary color development by having present substantive agents in the blue-sensitive emulsions so that both primary and secondary color formation together will yield a sufficiently heavy image.

[10] Homolka, *Phot. Korr.* **44** (1907) 55, 115.

[11] Fischer and Siegrist, *Phot. Korr.* **51** (1914) 18.

[12] *Brit. J. Phot.* **86** (1939) 120.

Secondary color development has become the accepted method of color formation in modern dye-building processes. The number of possible couplers for use with a few developing agents has increased rapidly during the last ten years. A listing of the classes of dye formation may be found in the literature. For a further discussion, see p. 304.

Control of Color Formation.—The localization of color formation in the various positions of an integral tripack follows two general patterns, the first of which depends on the differential processing of the various layers of emulsion, while the second method forms the colors by means of reagents already present in the proper emulsion layers.

Differential processing methods may be subdivided into those dependent on the controlled penetration of processing solutions and those dependent on some means of differential exposure of the emulsion layers. This line of demarcation is not too sharp as some methods cut across the line—such as those employing differential re-exposure by means of the controlled penetration of light!

Controlled Penetration Methods.—These methods of color formation are dependent on the fact that suitably prepared solutions penetrate into a layer of emulsion at a very slow and controllable rate. The average developer takes only a second or two to penetrate an emulsion layer of normal thickness but, if certain "loading" reagents such as alcohol, glycerine and sugar are present, the penetration period is greatly extended. For example, in the reversal of an integral bipack which has been developed and subsequently bleached, it is possible by means of a loaded dye coupling developer to redevelop the top layer of halide without affecting the lower emulsion, if the time of development is carefully controlled. The efficiency of such controllable penetrating solutions is greatly increased by the inclusion of gelatin-separating or filter layers between the emulsions. Whenever controlled penetration methods are to be used, the gelatin of the separating layers is chosen to give considerable swelling when wet. The employment of controlled penetration methods is not limited to developers since bleaching baths, resensitizing solutions and even light itself may be used. Controlled diffusion of the bleaching solutions was used for several years in the processing of Kodachrome film. The effect of controlled penetration may also be obtained by the application of normal solutions on a pack

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Tull—Brit. J. Phot. **85** (1938) 627, 647; **86** (1939) 115; **87** (1940) 17, 30, 39, 576, 587, 603.

Friedman—Am. Phot. **34** (1940) 914; **35** (1941) 62, 136, 220.

containing waterproof separating layers which could be removed after use. The necessity for even emulsion coatings is again evident when considering controlled penetration methods in relation to the aforementioned thin emulsions.

Differential Exposure Methods.—The second type of differential processing makes use of various means of exposing or processing the different emulsions separately and at will. For example, if a temporary opaque screen is obtainable on both sides of the center emulsion of an integral tripack, it is a simple matter to expose the bottom emulsion through the film base, the top emulsion from the film's front surface, and then to expose the center emulsion after the opaque screens have been removed. Differential exposure methods generally depend on some feature of the monopack's separating layers, or on the emulsions themselves, to make individual exposures feasible. For example, the separating layers may contain fogged silver salts which become opaque screens during the first development and therefore protect the center layer from light until the screens are removed after the second development of the outer two emulsions, or the separating layers may be various forms of color filter (even ultra-violet) which would prevent certain spectral regions from affecting the central emulsion. The same result may be obtained by making use of color sensitizers in the emulsions that remain effective *AFTER* the first development. This is the principle employed at the present time in processing Kodachrome. It is also possible to obtain the effect of differential exposure by the proper mixture of silver chloride and silver bromide emulsions since they are affected differently by a given developer, and with appropriate solutions they may be developed one at a time.

Use of Substances Fast to Diffusion.—If the emulsions themselves can be made to hold part or all of the color-forming substances through the initial processing stages, all the differential processing methods will be unnecessary since a single stage of color formation results in the appropriate color being obtained in each layer of emulsion. The first essential for these substances is that they remain in their proper location and do not wander through the film. Such substances must be insoluble in the processing solutions and remain fixed in position. Compounds which fulfill the requirement of remaining fixed to their support without mordants are called *substantive* materials. The term "fast to diffusion" covers many types of color formation, such as the types of dye incorporated in the emulsion layers of a dye destruction process, the couplers present in the emulsions for use in dye coupling development, dyestuff generators and accelerators. The application of some of these special components is indicated in connection with the Agfacolor, Kodacolor and Gasparcolor processes.

Dye Bleaching.—In general, dye bleaching processes are not thought of in connection with integral tripacks. However, since the usual bleach-out process (see p. 782) consists of three light-sensitive systems coated one above the other on a single support, it deserves attention in this section.

Bleach-out processes have been proposed in two physical forms. In the first instance, the three light-sensitive dyes or agents are coated one above the other on a single paper or transparent support. To prevent the diffusion of dye from one layer to another, dyes are generally carried in different media. Thus, one dye might be incorporated in a layer of collodion, the others in layers of gelatin. In the second type of process, the three light-sensitive agents are mixed together in one medium and then coated onto the support. The former method has been the more widely adopted because less difficulty is experienced in finding a set of dyes which will work satisfactorily.

Gasparcolor Film.—Gasparcolor film is at present being used only for the positive printing of cine color pictures but the procedure is typical of the chemical dye destruction process. The film itself is a two-sided integral tripack, although a normal integral tripack with the three emulsions on one side of the film support can be used. Gasparcolor is a direct process in that a negative is obtained from a negative, thus necessitating the use of three separation positives for normal color printing. Color separation negatives made by any method are satisfactory and, from each one, suitable black and white separation positives are prepared. These positives are used in printing onto the color film.

Gasparcolor film consists of two emulsions on one side of a film base, the one next to the support being sensitive to red light and dyed yellow before coating. The top emulsion is sensitive to blue light and is dyed magenta. The third emulsion, on the other side of the film support, is a blue-sensitive emulsion which has been dyed cyan (see Fig. 381). The colors of the dyed emulsions are the normal subtractive primaries and the sensitivities are arranged so that each emulsion layer may be printed separately. It must be noted that the emulsion sensitivities have nothing to do with the color separation. If the tripack is exposed from the top to the black and white color separation positive which was printed from the green separation negative, a negative latent image will be obtained. If this exposure is made with blue light, the exposure will be restricted to the upper emulsion because of the limited penetration of blue light into the yellow emulsion layer next to the film support. A positive from the red record separation negative may be treated similarly in exposing the cyan dyed emulsion from the opposite side of the support. This exposure is also made with blue light. The yellow dyed red-sensitive emulsion is then exposed, using red light, to the blue separation positive. This exposure is made through the magenta emulsion which, of course, transmits red light freely. Since the center emulsion is the only one sensitive to red light, a proper recording is obtained.

When the three-part exposure has been made, the Gasparcolor film is developed and fixed normally and, after being washed, is treated with a dye destroying bath of the type discussed on p. 805. This bath destroys the dyes in the three layers wherever there is a developed image and in strict proportion to the quantity of silver present. A final bleach to remove the silver, and a washing, complete the processing. Each emulsion layer now contains a positive dye image in one of the subtractive printing primaries. It will be noted readily that this process is dependent on the dyestuffs being fast to diffusion, of the correct hues, lightfast and yet susceptible to destruction by the proper chemicals in the presence of silver.

Agfacolor.—Agfacolor film is a culmination of the early work of R. Fischer. It is a typical integral tripack in which the color formation is based on dye coupling development and the color localization on the incorporation in the emulsions of coupling agents which are not harmful to the photographic emulsion and are fast to diffusion. Agfacolor is fast enough for camera exposure. It can be developed to give a negative in complementary colors from which prints on a similar three-layer positive film can be made. The material which has been made available for amateur use is developed to give a transparency directly in natural colors since a single second development is sufficient to produce the proper three subtractive printing colors in the monopack layers. The successful commercialization of this monopack was made possible by the production of suitable coupling agents and sensitizers which could be incorporated in the emulsion layers without diffusion.

Agfacolor film consists of three light-sensitive emulsions coated one above the other on a single film base. The order of coating is that generally employed, red-sensitive emulsion next to the film base, blue-sensitive emulsion on top. The central green-sensitive emulsion is separated from the top layer by a yellow layer .001 mm. thick. The emulsion layers are approximately .005 mm. thick. Each layer of emulsion carries a substantive coupling agent which will yield the proper colored image upon development. The top blue-sensitive emulsion carries a colorless yellow coupler, the center green-sensitive emulsion carries a magenta coupler, while the lower red-sensitive emulsion carries a cyan coupling agent. The couplers must be colorless and of such a character as to be readily soluble in the emulsion ingredients and yet remain fast to diffusion when once coated—even during processing.

Development of Agfacolor film is comparatively simple and consists of three essential steps. In the first step, the negative color separation latent images produced during exposure are developed in a developer which does not yield color-forming oxidation products. After the negative development is completed, development is arrested and the film is exposed to white light. When exposed, the film is developed in a color-forming developer (second step). In this stage, the positive silver images are developed simultaneously with the formation of dye images. After processing in the color-forming developer, all the silver halides in all layers are reduced to metallic silver. In the third and last step of the process, all metallic silver from each layer is removed with Farmer's reducer, leaving pure dye images in natural color.

Kodacolor.—Kodacolor film, introduced in 1942 by the Eastman Kodak Company, is an integral tripack material employing dye coupling development in the formation of the color images. The protected coupling agents employed in the emulsions differentiates this process from Kodachrome. The Kodacolor process yields a color print which is obtained by the development of the original film to a color negative, and the printing onto a similar tripack to produce the positive picture on paper.

The exposure of the Kodacolor film, at present available only in rolls balanced for daylight illumination, is normal for a medium-fast black and white negative material. The top emulsion layer of the film records the blue light from the subject, the center layer the green light and the lower emulsion the red light. When this film is processed in a developer of the dye coupling type, the oxidized developer reacts with the yellow-forming coupling agent present in the uppermost emulsion and a silver and yellow dye image results. In a similar manner, magenta and cyan dyes are simultaneously formed in the proper positions in the other two emulsions. This procedure yields a three-layered nega-

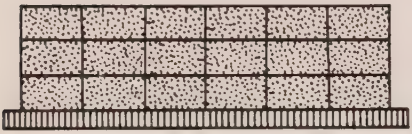
FIG 381

COLOR REPRODUCTION BY

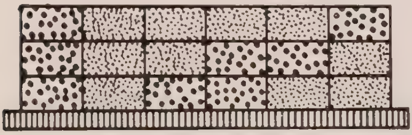
⬜ WHITE
⬛ BLACK
🟥 RED

░ SILVER HALIDE
● NEGATIVE SILVER IMAGE
○ POSITIVE SILVER IMAGE
▥ FILM BASE
▩ PAPER BASE

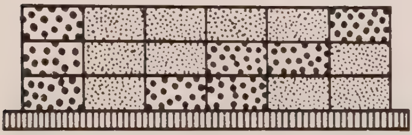
AGFACOLOR



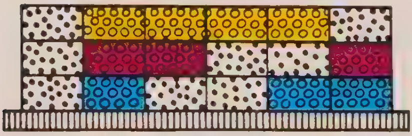
RAW STOCK. COLORLESS SUBSTANTIVE COUPLING AGENTS CONTAINED IN EACH EMULSION.



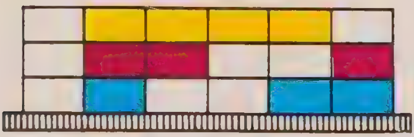
FIRST DEVELOPING WITH NON-COUPLING DEVELOPER. TOP LAYER RECORDS BLUE, LOWEST LAYER RED.



DEVELOPER REMOVAL FOLLOWED BY RE-EXPOSURE.



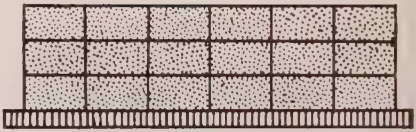
DYES FORMED IN PROPER LAYERS BY COUPLING REACTIONS.



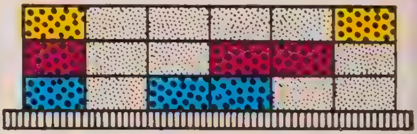
REMOVAL OF ALL SILVER.

INTEGRAL TRIPACK.
DYE COUPLING REVERSAL DEVELOPMENT.
COLOR LIMITATION BY SUBSTANTIVE COUPLERS.

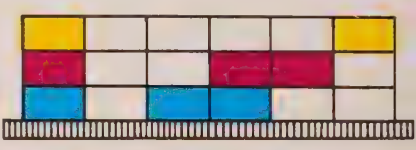
KODACOLOR



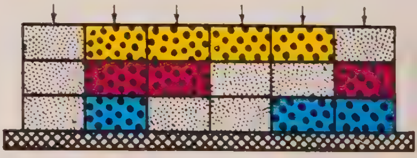
RAW STOCK. COLORLESS COUPLING AGENTS CONTAINED IN EACH EMULSION LAYER.



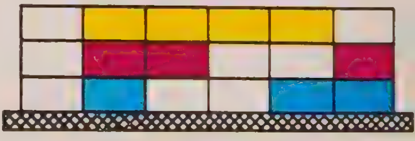
DEVELOPMENT WITH COUPLING DEVELOPER TO YIELD MINUS-COLOR DYE AND SILVER IMAGE.



SILVER REMOVAL LEAVING COLOR NEGATIVE TRANSPARENCY



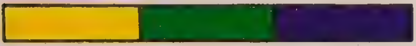
EXPOSURE AND DYE COUPLING DEVELOPMENT OF SIMILAR TRIPACK ON PAPER SUPPORT.



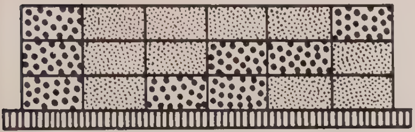
SILVER REMOVAL LEAVING POSITIVE COLOR PRINT.

INTEGRAL TRIPACK.
DYE COUPLING NEGATIVE-POSITIVE PROCESSING.
DYE COUPLERS INCORPORATED IN EMULSIONS.

COMMERCIAL TRIPACK PROCESSES

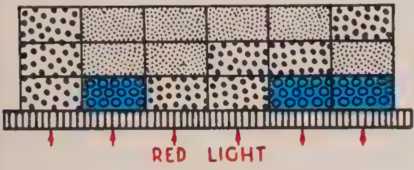


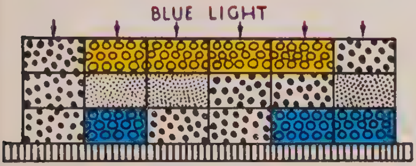
KODACHROME KOTAVACHROME MINICOLOR



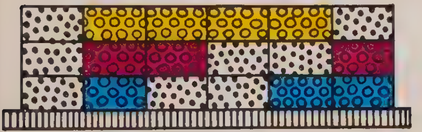
FIRST DEVELOPMENT. TOP LAYER RECORDS BLUE, CENTRAL LAYER GREEN, AND LOWER LAYER RED.

RE-EXPOSURE TO RED LIGHT AFFECTS ONLY LOWEST LAYER. CYAN DYE COUPLING DEVELOPMENT.

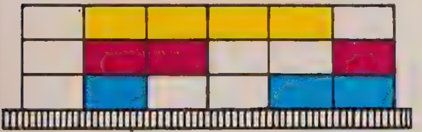




RE-EXPOSURE TO BLUE LIGHT. DYE COUPLING DEVELOPMENT YIELDS YELLOW DYE IN TOP LAYER.



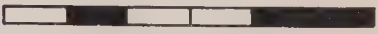
CENTRAL EMULSION DYE COUPLED TO YIELD MAGENTA DYE IMAGE.



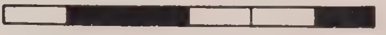
SILVER REMOVAL LEAVING DYE COLOR TRANSPARENCY OR PRINT.

INTEGRAL TRIPACK.
DYE COUPLING REVERSAL DEVELOPMENT.
COLOR LIMITATION BY DIFFERENTIAL RE-EXPOSURE.

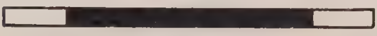
GASPARCOLOR



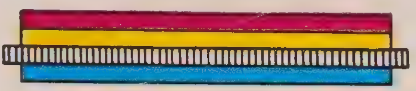
A POSITIVE FROM RED RECORD NEGATIVE.



B POSITIVE FROM GREEN RECORD NEGATIVE.

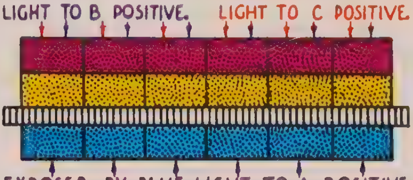


C POSITIVE FROM BLUE RECORD NEGATIVE.

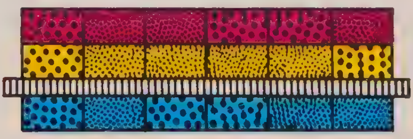


BLUE SENSITIVE EMULSION DYED MAGENTA.
RED SENSITIVE EMULSION DYED YELLOW.
BLUE SENSITIVE EMULSION DYED CYAN.

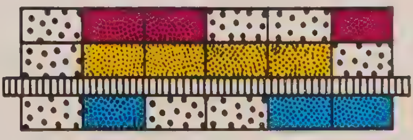
EXPOSED BY BLUE LIGHT TO B POSITIVE. EXPOSED BY RED LIGHT TO C POSITIVE.



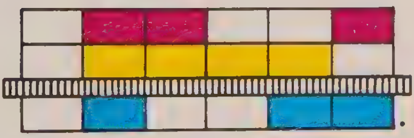
EXPOSED BY BLUE LIGHT TO A POSITIVE.



DEVELOPMENT OF THE SILVER IMAGES.



CHEMICAL DYE DESTRUCTION.



SILVER REMOVAL LEAVING POSITIVE DYE COLOR TRANSPARENCY.

TWO-SIDED INTEGRAL TRIPACK
CHEMICAL DYE DESTRUCTION.
SUBSTANTIVE DYES AND DIFFERENTIAL EXPOSURE.

tive silver image and a triple dye image formed simultaneously. The result is a color negative in that the chromatic as well as the achromatic areas appear reversed. Each colored object of the original scene is represented in the color negative by a dye or dye mixture of the complementary color. A red object will be reproduced as cyan, a blue as yellow. In the central emulsion layer, for example, wherever magenta dye is formed the emulsion has been affected by green light from the subject. After the silver images are removed, a color negative composed only of dyes remains. If such a negative is printed onto a similar material, a positive of the correct color is obtained (see Fig. 381).

The commercial introduction of an integral tripack negative-positive process for the production of color prints marks a worthwhile step forward. The increased latitude and higher color accuracy of a process of this type as compared with printing from positive color transparencies, make for reproductions of higher quality and consistency.

Kodachrome.—Kodachrome film is an integral tripack in which the color is obtained by dye coupling development during the latter stages of reversal processing. The segregation of the three subtractive colors is brought about by using in the various emulsions sensitizers which are not affected by the first development, thus making possible the differential re-exposure of the three emulsions by colored lights.

The evolution of this widely used type of integral tripack is based on the work of Mannes and Godowsky and the Eastman Kodak Company in the construction of monopack films. The commercialization of the process in 1935 followed the application of dye coupling development to these emulsions as the most satisfactory method of color formation. A single film base is coated with three superimposed emulsions, that next to the film base being sensitive to red, the top emulsion sensitive to blue and the center emulsion sensitive to green. The two upper emulsions are separated by a gelatin layer dyed yellow to prevent the penetration of blue light to the two lower emulsions. This yellow coloration is discharged during processing. After exposure, the film is developed in a normal developer to give black and white negatives in each emulsion layer. The limited spectral sensitivities of the different emulsions are retained during this stage of the processing, so the remaining halides are still sensitive to colored light in the same

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Brit. J. Phot. **88** (1941) 346.
Brit. J. Phot. **89** (1942) 122, 132, 170, 181.
Am. Phot. **36** (1942) No. 6, 40.

manner as before development. After the first development is complete, the film is washed to remove the developer and exposed to red light through the film base and developed in a dye coupling developer to yield a positive cyan dye image along with the silver positive. Because of the lack of red sensitivity of the two upper emulsions, the red light exposure is effective only in the lower emulsion. The film is then exposed to blue light from the top and developed in a dye coupling solution capable of yielding the proper silver-yellow dye image in the uppermost emulsion. The magenta positive image is obtained in the center emulsion by the employment of a dye coupler developer after fogging. A final bleaching of the silver in the three emulsions leaves three positive dye images in the proper subtractive colors. Kodachrome film was previously processed by means of the controlled penetration of bleaching baths. In this system, the emulsion sensitizers did not have to remain stable. The processing was more complicated, however, and has been replaced by the use of the differential re-exposure method.

Kotavachrome and Minicolor.—These identical processes were introduced by the Eastman Kodak Company in 1941. They are integral tripacks and the color formation is due to dye coupling development. For convenience in the standardization of the processing, the smaller-sized prints from miniature Kodachromes have been called Minicolor prints. The prints made from professional cut sheet Kodachromes are called Kotavachrome prints. The Kotavachrome prints are generally color corrected by a single negative mask (see Chapter XXXIV).

Kotavachrome and Minicolor differ from Kodachrome only in that the emulsions are coated on a white pigmented cellulose acetate base instead of on a transparent film support. This base acts as an efficient white reflecting surface and one which is convenient during processing and subsequent usage. The image contrasts of the three emulsions are lower than those of Kodachrome to make the result suitable for viewing by reflected rather than by transmitted light. Both materials are used by the Eastman Kodak Company in making color prints from Kodachrome transparencies.

CHAPTER XXXIV

ACCURACY OF COLOR REPRODUCTION

Introduction.—It would seem obvious that a color photograph should reproduce as accurately as possible all the colors of the original subject. In order to reach maximum usefulness such accuracy is particularly essential in the color reproduction of scientific subjects such as, for example, a clinical specimen. In the general field of photography, however, facsimile reproduction is not necessarily the most desirable state of affairs. The artistic requirements for a given photograph may make it advisable to purposely distort the colors in the reproduction. Such factors as color contrast and fatigue, the surround, and the nature of the viewing conditions may seriously affect the visual impression received by an observer. It is common knowledge, for example, that the human observer soon accustoms his eye to such varying color distribution illuminants as outdoor sunlight and indoor incandescent lamps, so that after a short period of adaptation objects seen under either of these illuminants appear perfectly normal.

Since practical color processes achieve their reproduction by means of a three-color analysis, it is obvious that a discussion of the accuracy with which colors can be reproduced by existing processes is in order. A color process capable of accurate reproduction is essential, at least theoretically, before intentional color alterations can be introduced. In general, the color processes available today have not been utilized to their fullest capabilities as to color accuracy, the majority of unsatisfactory reproductions being due to faulty manipulation rather than to any limitations imposed by the process itself.

The improvement in quality of color reproduction during the last thirty years has been chiefly due to improved techniques and the development of superior materials for carrying out the necessary operations. The basic methods of analysis and synthesis have seen very few innovations since 1900. There was a lack of accuracy of reproduction in the early processes but the difficulties were chiefly due to the

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Murray and Spencer—Colour in Theory and Practice, Vol. I, 1940.
Wright—Phot. J. **80** (1940) 25.
Southall—Introduction to Physiological Optics, Oxford, 1937.

inadequacy of available materials. As the quality of color reproduction has been raised, the foundations of three-color photography are being re-examined in an effort to improve present results and to indicate further lines of attack.

Colorimetry.—Any investigation into the accuracy of color reproduction must of necessity make use of some standard to which the results may be referred. The methods involved in the measurement and specification of color constitute what is known as Colorimetry. The fundamental basis of Colorimetry is that natural colors may be matched visualy by suitable mixtures of three primary colors. The primary colors chosen may be either narrow—essentially monochromatic—regions of the spectrum, or rather wide transmission areas; in either case, some combination can be found to match the unknown color. The amounts of the three primary colors necessary to match the unknown are called its tristimulus values. The tristimulus values for a typical tricolor red filter, for example, are $X = 635$, $Y = 315$, $Z = 0$. A set of tristimulus values may readily be converted mathematically into trichromatic coefficients or coordinates which are useful in showing graphically the characteristics of all colors. Two of the trichromatic coordinates serve to determine the location of any color on a chromaticity diagram. These two coordinates, along with one of the tristimulus values, serve to specify the three attributes of any one color in relation to all other colors. In the chromaticity diagram of Fig. 382, the trichromatic coordinates of a set of tricolor separation filters have been plotted as examples. The curved solid line represents the locus of the spectrum colors and W is the location of the white point on the diagram. As the position in the chromaticity diagram of any color moves from the vicinity of the spectrum locus toward the white point, the color tends to become less saturated. Complementary colors are on opposite sides of the white point. Trichromatic coordinates may be obtained by calculation from the results of color matches made in a colorimeter or by calculation from spectrophotometric curves.[1]

[1] The testing of the color accuracy of any reproduction or process must of course be referred to Colorimetry. The methods employed are discussed in the Handbook of Colorimetry and technical papers relating to Colorimeters and Spectrophotometers.

For a splendid discussion of Colorimetry and Spectrophotometry, subjects of growing importance in color photography, the reader is referred to Hardy, Handbook of Colorimetry, Technology Press, Cambridge, 1936.

MacAdam—J. Soc. Mot. Pict. Eng. **31** (1938) 343.

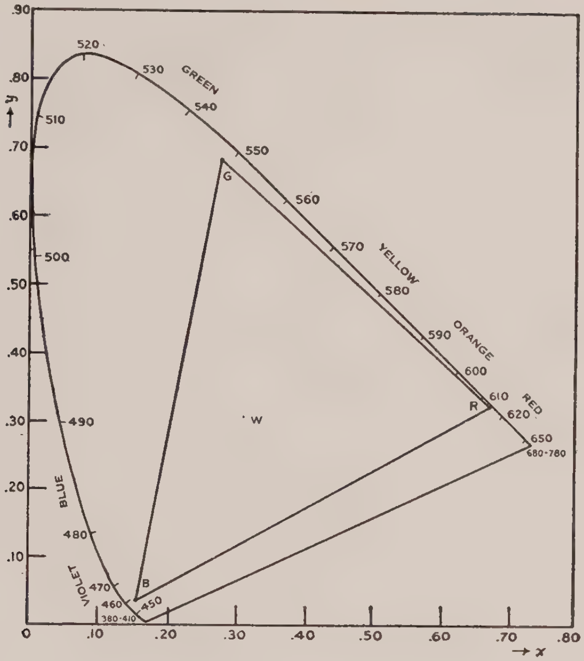

FIG. 382.

Additive and Subtractive Reproduction.—It is perhaps unfortunate that additive and subtractive color processes have been treated as two separate methods for the reproduction of color. Optically, these two ways of synthesizing a color analysis are identical. There is no difference in the visual appearance on the screen between a black and white positive projected through the red filter of a projection lantern and a cyan positive projected through the same red filter. In both cases the screen is black, red or some value of red, depending on the opacity to red light of the two positives. An additive synthesis is performed by projecting simultaneously the three appropriate black and white transparencies through red, green and blue filters with three projectors; while the subtractive synthesis is performed by the projection of cyan, magenta and yellow positives in one projector at the same time, by means of red, green and blue light which together form white. If the positives were made from the same analysis set of separation negatives and the subtractive colors, cyan, magenta and yellow, were ideal, the results of these two syntheses (using identical projection primaries) would be the same.

If the three filters shown in Fig. 382 were used for an additive synthesis, the colors that could be reproduced would be those lying within the triangle formed by the filters when plotted on a chromaticity diagram. While this triangle does not include all colors, the range is sufficiently great to include the colors of almost every naturally occurring object. The color gamut of a typical subtractive process is smaller than that shown in the chromaticity diagram due chiefly to the relative superiority of the available additive filter dyes over the coloring materials used for subtractive printing.

Subtractive Color Correction.—By far the largest quantity of color printing is done by means of subtractive color synthesis and this method must be employed to obtain a satisfactory color reproduction on paper. It is natural, therefore, that the greatest efforts have been expended in trying to overcome or minimize the color errors found in subtractive reproductions. All the early investigations were empirical in that attempts at correction of the observed deficiencies were made chiefly by trial and error. Since the greatest commercial interest was in color printing by means of inks (letter press, lithography and gravure), it was natural that the first corrective measures were developed for use in mechanical color printing rather than in purely photographic processes of color reproduction.

Need for Correction.—The necessity for correcting the colors of a reproduction arises from the fact that the three printing colors, cyan, magenta and yellow, do not reflect and absorb light in the manner required to make them optically equivalent to the additive red, green and blue colors. For example, the cyan image, when printed onto paper, should produce the same effect visually in red light as would a black and white slide projected by red light onto a screen, and the cyan image should disappear completely when viewed with green or blue light. The only purpose of the images in each case is to act as control valves for the red reflectances The cyan image should absorb red light completely and reflect or transmit the remainder of the spectrum for accurate reproduction and the maximum color gamut. An examination of the reflectance curve of the "ideal" cyan shows a complete absorption of red and complete reflectance of blue and green. Practical cyans, however (Fig. 383), depart from the ideal in that they do not absorb red completely, and, of more importance, they do absorb a very large portion of the blue and green they are supposed to reflect. The "ideal" magenta should be a perfect absorber of green and should reflect the remainder of the spectrum, namely, red and blue. Obtainable magentas do not absorb green completely and are far from satisfactory reflectors of blue.. Most yellow printing colors, on the other hand, are satisfactory enough for practical purposes. The inefficient red absorption of the cyan and the inefficient green absorption of the magenta are secondary defects and may be ignored as a first approximation, but the poor green and blue reflections of the cyan and the poor blue reflection

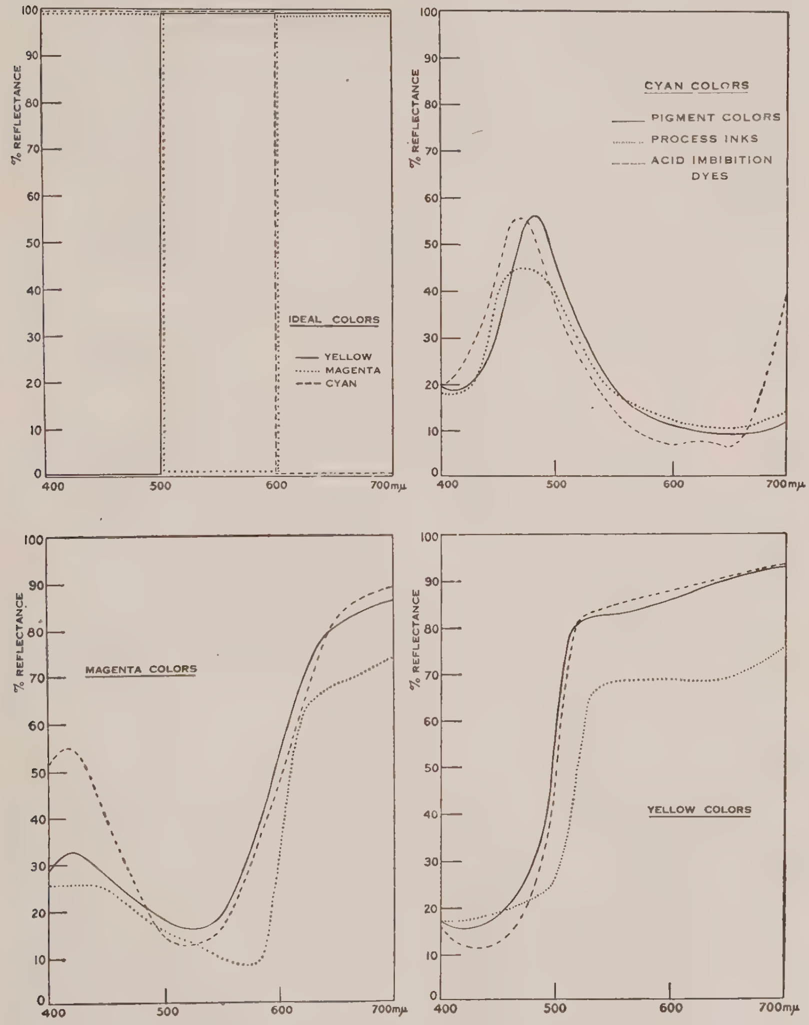

FIG. 383. Ideal and Real Reflectance Values for Subtractive Printing Colors.

of the magenta are serious enough to cause noticeable reproduction errors. It is evident from the character of these typical printing inks why printers have used the terms blue, red and yellow in naming their printing colors. In fulfilling the necessary press and light fastness requirements, the available inks do not approach the desired cyan, magenta or yellow hues.

Effect of Normal Printing Colors.—The result of using available printing inks leads in general to a darkening of the cold colors and a desaturation of the warm colors. In Fig. 384, where five colors and their reproductions have been plotted on a chromaticity diagram the color shifts may be readily observed. Examination of the defective blue reflection of a typical cyan shows that when this ink is printed to deposit red densities on the paper support (absorption of red light), it also deposits a certain percentage of blue density (absorption of blue light). The same situation exists for the magenta where the printing of green densities involves, because of the deficient spectral reflection, the print-

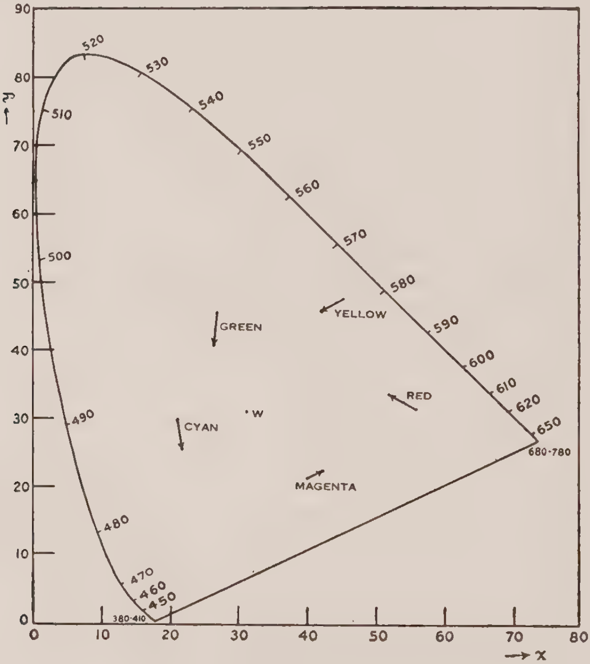

Fig. 384. Five Colors (Dots) and Their Reproductions, (Arrow Heads) Plotted on a Chromaticity Diagram.

ing of blue densities. Since it is the yellow ink that is *supposed* to print all the blue densities in the reproduction, the amount required to produce a neutral gray scale (composed of equal parts of red, green and blue densities) is considerably decreased. The quantity of yellow printing in all areas of the picture is of course dependent on the amount of yellow required by the gray scale. This situation leads, therefore, to lesser deposits of yellow ink than are required for accurate reproduction of all yellows and colors containing yellow in the chromatic [2] areas of the picture—a desaturation or dilution with white. The same situation for the magenta is brought about by the undesirable green densities deposited by the cyan ink and all colors containing magenta and yellow are therefore less saturated than desired. On the other hand, the poor reflection of the blue region of the spectrum by both the cyan and magenta and the poor reflection of the green by the cyan ink leads to a rather limited brightness for blues, greens and their mixtures in a color print.

Corrective Measures.—The deficiencies noted cannot be corrected by the simple expedient of changing the contrast of one or more of the printing colors since any slight improvement brought about for some particular color would be offset by a further loss of color accuracy in some other colors. An empirical approach to correction may be made in two directions. In the first place, a study of the spectrophotometric curves of the printing inks indicates that improved color reproduction will be obtained by a decrease in the amounts of yellow and magenta in all areas of the print where cyan is required. In this manner, the extra blue and green densities deposited by the cyan ink are partially corrected. The second method of approach to the problem is to consider the reproduction of a picture made from the three printing inks. If a correct reproduction of such a picture can be made, i.e., if each of the three printers deposits the same amount of ink as was present in the original picture, it is reasonable to suppose that reproductions made under the same conditions of other types of original would be fairly accurate.

The employment of such corrective measures will lead to a very considerable improvement in the accuracy of color reproduction. In photo-mechanical processes, the corrective measures may be applied by hand. After the metal plates have been proofed, the magenta and yellow images are locally etched to decrease the amounts of magenta and yellow inks printing in areas where cyan is deposited on the picture. Successive proofs and local etchings are carried out until the desired correction is obtained. Since the extent of the corrections necessary is *not* dependent on the subject matter but only on the characteristics of the printing colors employed, the correction for any given density of a particular color will always be the same. It is therefore possible to employ photographic means to obtain the desired corrections. Photographic color correction, or masking, involves the alteration of the density distribution of a given negative or positive by binding in contact with it another positive or negative. This mask may be used to alter either the contrast or the contrast and the color separation values. Photographic color correction as normally carried out will not lead to perfect color reproduction since only the larger defects can be satisfactorily corrected. To be commercially feasible, the number of corrective operations must be kept to a minimum, and since the errors it is desirable to correct are not of equal magnitude, simple masking will not lead to facsimile reproduction but can give greatly improved results.

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[2] Chromatic colors are those distinguished by hue (red, yellow, blue, etc.). Achromatic colors are those without hue (grays, white, black).

A system of photographic color correction described by Murray is typical of the procedure followed.[3] A normal red separation negative is exposed and developed. The green and blue separations are made having density ranges 1.6 and 1.4 times that of the red negative. From the red record negative, two positives are made having density ranges of 40% of the green record and 30% of the blue record.[4] These positives are bound with the green and blue separations to form the color corrected negatives. The positive masks on the green and blue record negatives prevent some magenta and yellow from printing in those regions where cyan is present, thus decreasing the degradation of cyans, blues and greens. At the same time, the increased contrast of the magenta and yellow images (neutralized by their masks for all neutral or achromatic tones) leads to a higher saturation (increased printing strength) of all reds, yellows and magentas.

Black Printers.—The superimposition of three normal process inks leads to very poor reproduction of detail in the dark neutral areas

[3] *The Modern Masking Method for Correct Color Reproduction,* Eastman Kodak Co.

[4] Such masking methods are not the best obtainable but were the first strongly advocated commercially. It must be borne in mind that these procedures were developed empirically before the applications of Colorimetry and the Subjective Theory of Color Reproduction indicated the proper method of color correction.

An excellent review of photographic masking methods, mostly for use with printing inks, was given by Tritton, Phot. J. **78** (1938) 732.

of the picture. The maximum neutral density obtainable is about 1.3. Wherever higher densities are required, the tendency is for the neutral tones to become colored, generally reddish. For this reason, printers have been led to use four-color processes for quality reproduction, making use of the three standard subtractive colors and a fourth black impression. There are two uses to which the black printer can be put. In the first case, it can be used to print only on the dark neutral areas of the print, so supplying the necessary additional deposits to make possible achromatic detail in densities greater than 1.3. In the second place, the black printer can be used to supply *all* the neutral tones of the picture, whatever their density, as well as the gray component for all chromatic areas requiring it.

The first suggestion for a black printer seems to have come in 1897 from Albert,[5] who suggested the removal of the achromatic components from each color impression in the final print so that the three color printings supplied only the chromatic portions of the picture. A fourth printing supplied all the black to the reproduction. A black printer of this type, supplying all the achromatic portions of the picture, greatly improves the photograph because of the absence of any difficulty in properly balancing the three chromatic colors at all densities—in ordinary practice somewhat difficult to accomplish. This use for a black printer is especially desirable for three-color photographic printing as well as for printing inks. The second type of black printer involves the printing in of achromatic areas of densities greater than can be satisfactorily reproduced by the three printing colors alone. The negative for such a printer is generally exposed through a yellow filter on panchromatic material. If a normal density printer is made from this negative, the black will degrade all the color areas of the picture. To avoid this difficulty, the black printer positive is only lightly exposed, thus limiting its deposits to the shadows. Considerable hand corrective work is generally necessary even with such an expedient. Murray suggested an improvement (for certain specified types of copy) by recommending an infra-red separation negative for making the black printer.[6] The applicability of the infra-red method is dependent on the fact that most coloring materials strongly reflect infra-red while many achromatic materials absorb infra-red radiation. Thus, a black printer made

[5] D.R.P. 101,379.

[6] Murray, *National Lithographer* **41** (1934) 19; *Photo-Engravers Bull.* **23** (1934) 13; **24** (1935) 208.

from an infra-red record will not deposit black on any but achromatic areas. Yule [7] has recently shown that the densities of the black printer should be related to the lowest equivalent density of the three color components when suitably color corrected and, for the most accurate reproduction, a mask from such a black printer should further correct each of the color corrected separation negatives.[8] Black printers are rarely used in strictly photographic reproduction methods since the combined dyes or pigments yield satisfactory neutral images—the improvement in color accuracy does not generally justify the extra operations.

Other Photographic Color Correction Methods.—The amount of color correction required for most photographic color printing methods is not so great as that needed for printing inks because of the somewhat superior spectral absorptions of the printing colors. As shown in Fig. 383 the deficiencies of the various magentas, for example, vary somewhat, and for the fullest color correction the extent of the masking required should be determined for the process employed.[9]

It is possible to increase the sharpness of divison between the areas of the picture printed by the three printing colors by the use of weak positives obtained from negatives made with "minus color" filters (cyan, magenta and yellow) as masks in contact with the normal separation negatives. In this manner, the areas printed by any given color are restricted by the mask. This method is not so widely used as some of the other masking procedures discussed.

In general, it may be stated that some correction is desirable in almost every case. The extent to which masking should be carried is dependent on the presence of colors that would be poorly reproduced without corrective measures, and the necessity for high color accuracy. It is better to undercorrect than to carry the masking to extremes, both from the standpoint of color accuracy and the "photographic quality" of the reproduction. The physical combination of negatives and positives of fairly high contrast leads to difficulties with image spread at the outlines of objects and a general destruction of tone. Optical means for carrying out the masking operations have been suggested [10] to overcome these difficulties, but they are expensive and hard to operate. Corrections may also be made electrically [11] or by means of special photographic emulsions or copy coloring materials [12] which automatically give the desired masking effect. (See also Chapter 33.)

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[7] Yule, *J. Opt. Soc. Am.* **30** (1940) 322.

[8] *Brit. J. Phot.* **87** (1940) 99, 112.

[9] Colton, *Phot.Tech.* **1** (1939) No. 3, 19.

[10] *Klimsch's Jahrbuch* **29** (1936) 67.

[11] *Brit. J. Phot.* **86** (1939) 259; **87** (1940) 112.

It is possible to employ colored images as masks. The density of the colored image to the light-emulsion combination employed determines the extent of the correction obtainable with a given mask. A method suggested by Kodak [13] for use with the Wash-off Relief process involves the making of a relief film from the red separation negative and its dyeing to the proper contrast in the cyan dye. This relief film is combined with the green separation negative, and the combination used in exposing the relief film to be dyed magenta. The density of the cyan dye to blue light gives considerable color correction for the magenta image. After dyeing the magenta, the combination of blue separation negative and cyan and magenta positive images is used in exposing the relief film to be dyed yellow. This method does not give full color correction and is rather difficult to use except for contact printing, but because of its low cost (no extra materials necessary for use as masks) and worthwhile correction, it has found widespread usage.

The theoretical color corrections required for a set of acid imbibition dyes has been calculated and various simplified approximations originated that cover the larger errors of reproduction. For example, it has been shown that the red filter negative should be masked by a positive from the green filter negative; the green filter negative should be masked by a positive from the red filter negative; the blue filter negative should be masked by a positive from the green filter negative. Various two-mask methods have been calculated since the most important masks are the red filter masking positive on the green record negative and the green filter masking positive on the blue filter negative. Selman [14] has published details of three distinct procedures for obtain-

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[12] Automatic color correction may be obtained optically by exposing the color separation negatives through, or subduing the copy by means of, negative masks. If copy is being colored for subsequent photographic separation, special paints such as the Kodak Fluorescent Paints that fluoresce under ultraviolet illumination may be employed. After the color separations have been exposed in the normal manner, supplementary exposures by means of ultraviolet light fluorescence add density to the negatives requiring color correction. Figure 381 was prepared with Fluorescent Paints and the reproduction plates did not require any additional photographic or manual color correction.

[13] Color Printing with Eastman Wash-off Relief Film, Eastman Kodak Co.

[14] Selman, *Phot. J.* **80** (1940) 375.

MACADAM—J. Opt. Soc. Amer. **28** (1938) 466.
MARRIAGE—Phot. J. **80** (1940) 364.

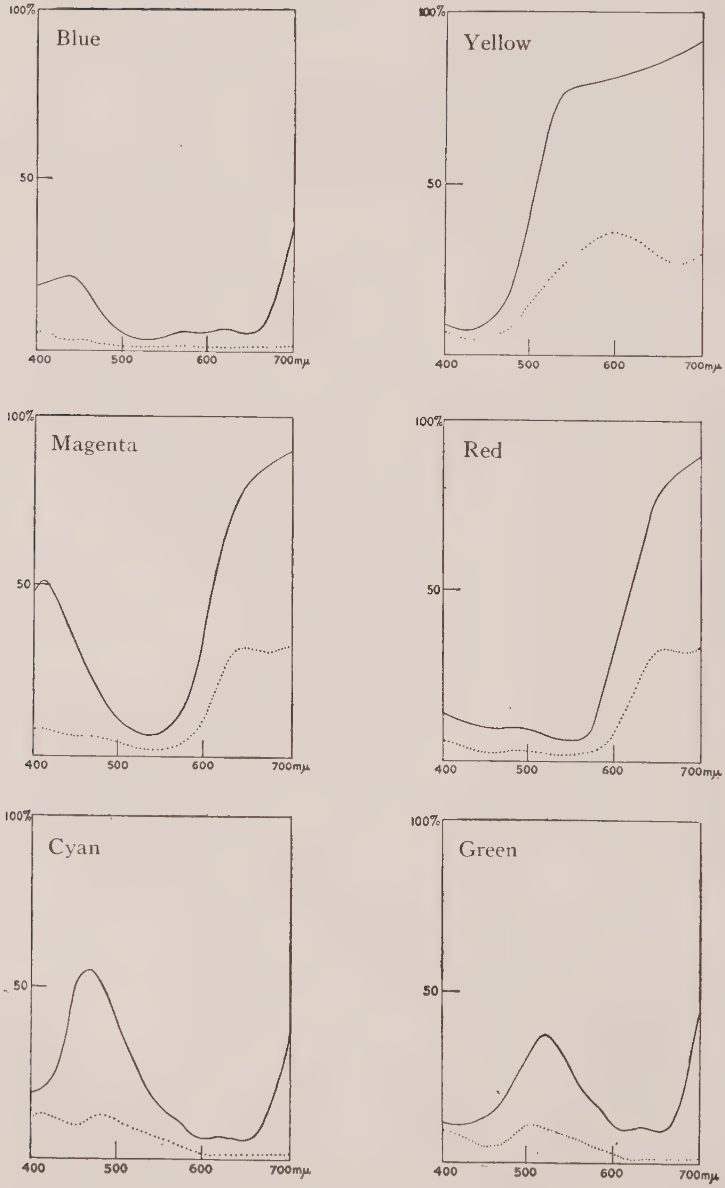

Fig. 385. Original (Solid Lines) and Positive Color Transparency Reproduction (Dotted Lines). Spectrophotometric Curves of Six Bright Colors.

ing satisfactory correction for Wash-off Relief dyes, two using the silver relief film images as masks and a third using standard positive images.

Accuracy of Color Transparencies.—Color transparencies of the screen or integral tripack types are used for direct printing, projection or as a means for obtaining three color separation negatives for subtractive color printing. The accuracy of reproduction of screen materials was discussed in Chapter XXXII and this section will deal more specifically with integral tripacks.

A color transparency considered by itself, thereby disregarding errors due to improper exposure and processing, may not be an accurate reproduction of the original scene because (1) the limited latitude of the reversal process involves inaccurate reproduction of all but a fairly short range of subject luminosities, and (2) the spectral absorptions of the dyes composing the three positive color images are not ideal. The extreme brilliance of the average color transparency leads to its psychological acceptance as an accurate reproduction of the original scene. Colorimetric measurements, however, show very definite inaccuracies in the transparency. In Fig. 385, for example, the spectrophotometric curves of the original colors and their transparency reproduction are considerably different, yet the eye will accept such a transparency as a good match.[15] The acceptance of such color errors is not of vital importance until it is necessary to make a color print from the transparency.

Roles of the Color Transparency.—Printing from color transparencies involves the preparation of a set of three separation negatives to be printed in the usual manner, or the direct printing onto materials of the dye bleach, dye destruction or dye coupling types. The color transparency may be considered either as an original color picture to be photographed or as a set of physically inseparable colored separation positives or negatives. One desired goal is the accurate reproduction of the positive color transparency. Such a result requires similar dyes in similar amounts at each point of the reproduction as was present in the color transparency. A second method seeks to obtain a reproduction of the original scene from which the transparency was made.

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[15] These curves, incidentally, show the vital importance of proper exposure for the color it is necessary to reproduce accurately. All five colors received equal illumination, but for the best reproduction of the violet and green a greater exposure would be advisable. Such an increase would have decreased the accuracy of reproduction of the lighter red, yellow and pink color patches. The colors shown are special cases and should not be interpreted as a general case. Most less saturated colors would be reproduced considerably better. The differences would not be quite as marked if plotted on a Chromaticity diagram.

Reproducing Color Transparencies.—Indirect reproduction from color transparencies necessitates the use of a set of color separation negatives made from the color film. The color filters generally used are of the analysis type (sharp cutting filters without appreciable overlap) such as Wratten Numbers 29, 61 and 49. The panchromatic emulsion to be used should be carefully chosen (1) to have as long a straight portion to its characteristic curve as possible, (2) to have curves of similar shape for each separation and (3) to have a sensitization of the medium red sensitivity type. Exposure, by contact or projection, and development are carried out normally so that a neutral gray scale is recorded equally on the three separation negatives. The chief difficulty in the reproduction of positive color transparencies by this method lies in the excessively long brightness range of the film's color image to be reproduced. As most of these materials are intended for projection, the contrast is very high. The average minimum density is approximately 0.3 and the maximum 3.00, a density range of 2.70. When separation negatives are made from such a subject, color distortion results because of the inability of the negative materials to record such a density range on the straight line portion of their characteristic curve. Exposures long enough to record transparency densities as high as 3.0 onto the separation negatives are generally so long that the lower densities are recorded with excessive image spread and halation—thus leading to a loss of photographic quality.

Since accuracy of highlight detail is most important, the separation negative exposures are arranged so that the highlight densities of the transparency fall near the break between the straight line and the shoulder of the characteristic curve of the material employed,[16] as in Fig. 386. Even with such placement, the shadow regions of many color transparencies will be incorrectly reproduced because they are recorded on the toe portions of the separation negatives. Development to a low contrast ($\gamma = 0.6$) is necessary to keep the reproduction scale within the range of the negatives and the printing process to be subsequently employed. The density range of the color transparency may be reduced, and so minimize the difficulty, by using a low contrast black and white negative bound in register with the color transparency while the separation negatives are being made. This negative mask is printed by contact with the color transparency, using a panchromatic emulsion and white light.[17] After developing to a low contrast and drying, the mask enables the density range of the transparency-mask combination to be readily recorded on the straight region of the separation negative characteristic curves. Direct positive dye images may also be obtained from color transparencies (page 779).

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[16] Kurtzner and Seymour, *Amer. Phot.* **32** (1938) 862.

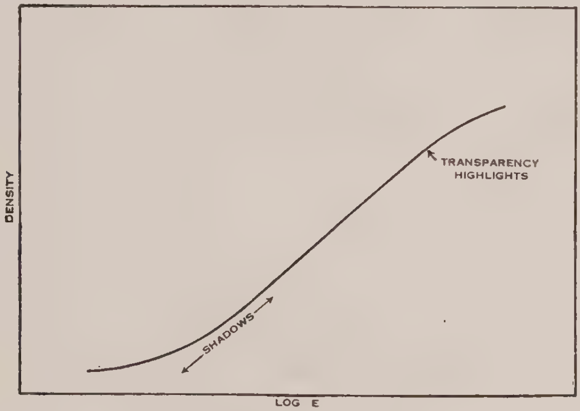

Fig. 386. Placement of Transparency Highlights at Negative Characteristic Curve's Shoulder May Enable Shadow Areas to Record on Straight Line.

Inaccuracies of a Color Print.—If a satisfactory set of color separation negatives, made as discussed above, is printed by any of the subtractive paper print processes, the reproduction usually proves to be a great disappointment. This failure is due to three factors:

1. The reproduction of the transparency as a print.
2. The unsatisfactory spectral absorptions of the printing colors employed.
3. The transparency's not being the same as the original. (Colorimetric view of equality.)

The inherent limitations of a paper print as compared with a transparency, whether in black and white or in color, cannot be too strongly emphasized. Because of the limited brightness range which a print viewed by reflected light is able to reproduce satisfactorily, the gradation of a considerable portion of all but very short scale subjects is incorrectly recorded. For example, by means of color correction, it is possible to reproduce the original color transparency very accurately as a set of imbibition matrices dyed to be examined by transmitted light. If these same matrices are lowered in contrast to make them suitable for viewing by reflected light, the reproduction will be correct only over a very limited range. It is important to note that the color accuracy is in the matrix images but simply cannot be seen by reflected light.

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[17] Such a procedure is not the same as using a low contrast method since the mask maintains color saturation but reduces the achromatic scale.

The discussion on p. 818 of the inefficient spectral absorptions of printing colors applies to the reproduction of color transparencies, and to obtain color accuracy, some of the masking correctives must be employed. The color correction should be as complete as possible because the other errors just discussed, which cannot be eliminated, will cause sufficient color degradation. Suitable masking will enable a quite faithful *transparency* reproduction of the original color transparency to be prepared.

The third difficulty is dependent on the memory of the observer for the original scene as compared with the color print. The color transparency is not, of course, an accurate picture of the original scene, since it suffers from all the defects of inefficient spectral absorptions of the dyes composing the three positive images in the transparency. Recent developments indicate an increasing use of partial automatic masking during the processing of positive color transparencies. In this manner it is possible to produce reasonably accurate reproductions of the original. An accurate reproduction of the transparency, when in the form of a paper print, has had removed the psychological acceptance of the colors due to the extreme brightness range, and therefore the color errors are more apparent. It is not surprising, therefore, if a straight reproduction from a color transparency bears little resemblance to the original copy. It is in reality an inaccurate reproduction (print) of an inaccurate reproduction (integral tripack) printed within the limitations imposed by the brightness range of a paper print! Masking, as discussed above, will neutralize the errors of the printing process but will not remove the other deficiencies.

Recording Transparency Color Records.—A further improvement can be made by recording the color analysis performed by the tripack of the original subject. If the layers of the integral tripack were properly sensitized[18] so that each layer recorded one of the color separations, it would be desirable to take the separations apart physically. If this could be done with a knife, for example, three separation negatives or positives, equivalent to those that might have been exposed in the normal manner by successive exposures in a view camera, would be obtained. This desirable result would obviate all the difficulties arising from the inaccurate reproduction of the original scene by the transparency dye images. Such a procedure is feasible if done optically. The green separation record, for example, exists in a positive color transparency as the positive magenta dye image.

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[18] The color analysis by the tripack layers may not be so perfect as that obtainable by the usual trichromatic analysis but the errors introduced are of the second order and may be ignored.

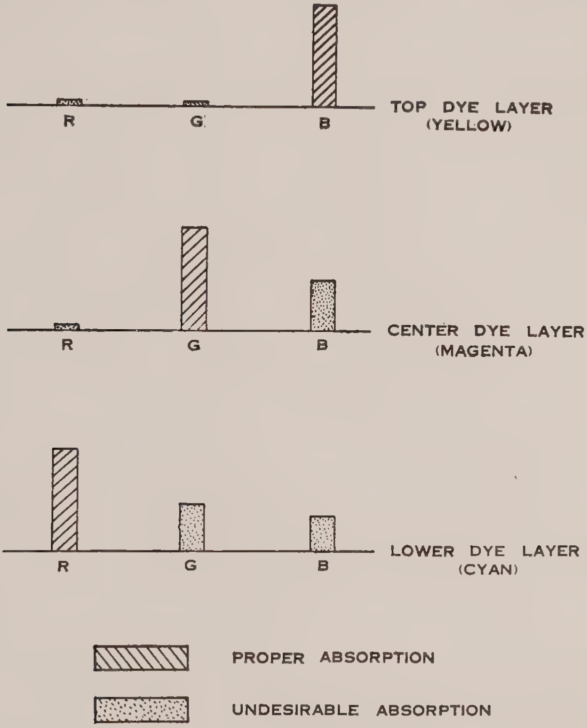

Fig. 387. Proper and Undesirable Light Absorptions by Typical Integral Tripack Dye Images.

If this image could be recorded on only one separation negative, the equivalent of the original green separation record would be obtained. Unfortunately, as shown in Fig. 387, all cyan and (to a lesser extent) yellow dyes show considerable absorption of green light and therefore will also be partially recorded on the green separation negative in accordance with their absorptions of green light. See also Fig. 383. In a similar manner, it can be shown that the red and blue separation negatives will record more than the desired cyan and yellow dye images respectively. The problem of obtaining a set of color separations from an integral tripack, therefore, resolves itself into the problem of recording each of the dye layers separately without interference from the other two.

Single Color Separations.—The recording of undesirable *positive* transparency images can be prevented by neutralizing the offending images with *negatives* of like color and contrast.[19] A red filter negative exposed in contact with the transparency, will, for example, record the cyan dye layer. This black and white negative may be converted into a negative cyan image with a contrast equal to that of the tripack positive cyan image. When these are bound together, the cyan tripack image is ineffectual while the blue or green separation negatives are being exposed. In a similar manner, a negative magenta mask will neutralize the effect of the tripack's magenta image. If the two masks and the color transparency are registered together, the blue separation negative obtainable from the combination will be approximately the equivalent of a color separation negative exposed to the original copy. Similar corrective masks may be applied when making the green and red separation negatives, although it must be borne in mind that the correction desired is not the same for each color.

Negative Silver Masks.—Another method leading to a similar separation makes use of negative silver image masks.[20] A negative of the color transparency made with a magenta filter, for example, records the cyan and yellow images (the red and blue separations in the tripack). If such a negative of the correct contrast is bound in register with the color transparency while the green record negative is being made, only the magenta dye layer image will be recorded for the green separation. In a similar manner, negative masks exposed through cyan and yellow filters are employed to allow correct red and blue separations to be procured.[21] This procedure has the additional advantage that the density range of the transparency is reduced, thus allowing the whole scale to be recorded on the straight portions of the separation emulsion's characteristic curves without excessive image spread and halation.

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[19] *Brit. J. Phot.* **86** (1939) 279. B.P. 494,341.

[20] Hoeppner and Paschel, *Modern Lithography,* Oct. 1939.

[21] Strictly speaking there are, of course, improper densities recorded on the negatives to be used as masks and the corrective measures necessary for the two undesirable dye layers in any given case will not be identical. These errors are of a second order in importance and may be ignored in practice.

Single Mask Method.—The previous methods require three negative masks with the necessity of registering the appropriate mask with the transparency before each of the color separation negatives is exposed. The possibilities of registration errors and a considerable loss of photographic quality are therefore present. A simplified procedure involves the use of but one negative mask to be bound in register with the transparency while the three separation negatives are exposed. This will allow the same scale decrease possible with the three mask method, a slight color correction, and only involve one-third the expense and difficulty. The filter used in exposing the mask may be almost any color depending on the correction desired. Both yellow and red have been suggested for landscapes and portraits respectively, but for all subjects combined together, the single mask exposed with an orange filter seems to give the best all around correction. As in the case of the three mask method, the contrast of the masks is dependent on the correction desired but must always be kept so low that no reversal from a positive to a negative occurs when the mask is bound with the color transparency. Recently introduced stripping emulsions that may be cemented onto the color transparency before being exposed and developed, make the single mask procedure quite simple and remove any difficulties with registration.

Supplementary Printing Correctives.—It must be borne in mind that the negative masking just discussed is designed to eliminate the errors introduced by the spectral absorptions of the dyes comprising the transparency images so that three pure color separation negatives may be obtained. If these three separation negatives are to be printed by the normal subtractive methods onto paper, the necessity of color correction for the spectral deficiencies of the printing colors still exists. If this is properly carried out by any of the normal procedures, the color reproduction obtainable from a color transparency closely approximates that obtained directly from the original subject.

Developments in Color Theory.—The foundation on which Maxwell based his original work on color reproduction was the three-color visual mechanism proposed by Young. The experimental visual color mixture curves presented by Maxwell and other workers were, for a time, thought to supply the clue as to the proper type of color analysis and synthesis necessary for satisfactory color reproduction. The mixture curves were obtained from experiments on the visual matching of spectral colors by means of three essentially monochromatic primary lights, colored red, green and blue. The exact colors chosen as primaries were not of vital importance as most colors could be matched by several suitable sets of primaries. Maxwell assumed that the photographic emulsion integrated, by means of its sensitivity and the transmission of the filter employed, all the energy falling on it so that its color record was that shown by the positive portion of the appropriate color mixture curve. This viewpoint was strongly supported by Ives[22] among others, but was soon displaced by a purely objective view of color photography.

The subjective viewpoint, i.e., that the observer's visual system was of basic importance, was discarded because of the belief that spectral color mixture data were not applicable to color photography. Serious questions were raised as to the exposure summation by the photographic emulsion and it was found that, if the color records were to follow the color mixture curves, the final synthesis should be made with monochromatic lights—a situation impractical in most cases. To be visually satisfactory as to brilliance, the additive synthesis colors would have to cover the spectrum, each color being roughly one-third of the visible region. When such colors are used for color vision experiments, the mixture curves exhibit much larger negative portions than those shown in Fig. 388, which are obtained from monochromatic mixtures. Since the problem in color photography is to reproduce natural colors of wide spectral reflectances instead of spectral colors, it was considered ad-

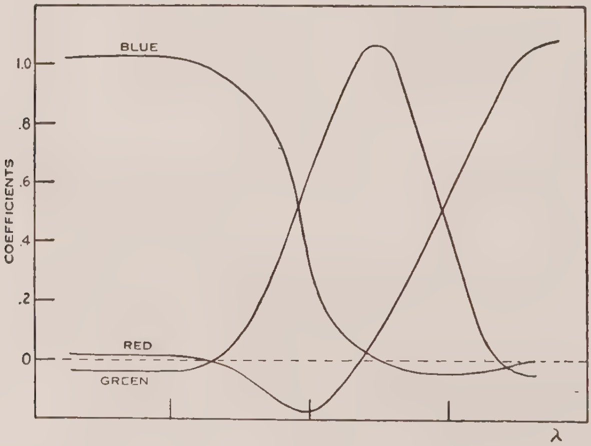

Fig. 388. Typical Color Mixture Curves.

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[22] Ives, *J. Franklin Inst.* **125** (1888) 345; **127** (1889) 54.

visable to base color reproduction on the practical color analysis filters which would merely determine the regions where the complementary colors were to print. A set of wide overlapping color curves were presented by Bull (see p. 746) as the ideal requirements for color analysis filters.[23] This objective viewpoint gained wide acceptance and directed most color work until 1930. The errors that were apparent in color reproduction [24] were readily explained as due to the unsatisfactory spectral absorptions of the subtractive printing colors and improvements in this direction were regarded as being of greater importance than further attempts at perfecting the analysis filters.

In 1935 Spencer [25] carried out an exhaustive series of experiments on the effect of various types of analysis color filters on the accuracy of subtractive color reproduction, and observed that the more closely the color filters came to corresponding with the "ideals" demanded by the objective theory, the less satisfactory the reproduction of color. Spencer pointed out that the commercial filters in common usage (which were designed to approximate the ideals as closely as possible) gave better reproduction in that they did *not* fulfill the ideal requirements. Indeed, the commercial filters were somewhat closer to the positive portions of the color mixture curves. At about the same time an investigation by van Kreveld [26] established the additivity law for photographic exposures [27] as demanded by the original concept of Maxwell. Such discoveries, along with the rapid improvement in color materials, naturally led to a new series of investigations into the theoretical basis of color photography.

Theory of Additive Three-Color Photography.—The theory of three-color photography has recently been under investigation by a number of workers, among them Schaefer and Ackermann, Neugebauer, Hardy and Wurzburg, Harrison and Horner, MacAdam and Yule. These investigations emphasize the subjective theory of color photography in that they are based on the color mixture data of the average human observer.

The goal of color reproduction is to obtain a visual match between the print and the original subject. This does not imply that the spectrophotometric energy distributions will be the same but merely that the visual appearance of the subject and reproduction will be identical. The visual identity of two colors occurs when they have proportional tristimulus values. Hardy[28] has shown that the effective spectral sensitivities (sensitivity of emulsions and filter transmissions) of the analysis system are directly related to the color mixture curves of the observer and the colors to be used in the synthesis. This follows from Hardy's equations.

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[23] *Phot. J.* **51** (1904) 148; **52** (1905) 448; **75** (1935) 71, 258.

[24] *Phot. J.* **63** (1923) 403.

[25] Spencer, *Phot. J.* **75** (1935) 377.

[26] van Kreveld, *Z. wiss Phot.* 32 (1934) 222.

[27] Webb, *J. Opt. Soc. Amer.* **26** (1936) 12.

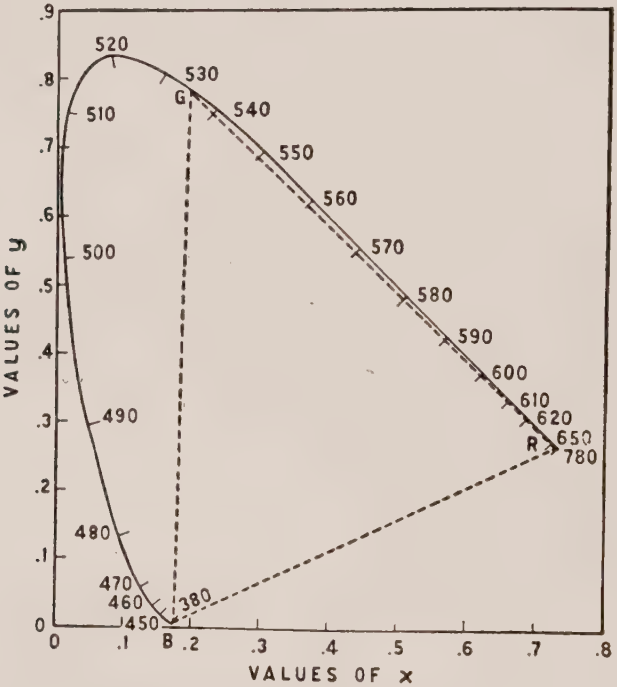

FIG. 389A. Color Gamut Obtainable with Positive Amounts of the Indicated Homogeneous Primaries Shown Inside Dashed Triangle. (Hardy, *J. Opt. Soc. Am.* 27 (1937), 227.)

$$\bar{x} = x_r S_r + x_g S_g + x_b S_b,$$
$$\bar{y} = y_r S_r + y_g S_g + y_b S_b,$$
$$\bar{z} = z_r S_r + z_g S_g + z_b S_b,$$

where $\bar{x}$, $\bar{y}$ and $\bar{z}$ are the distribution functions of the standard observer adopted by the International Commission on Illumination.

[28] Hardy and Wurzburg, *J. Opt. Soc. Amer.* 27 (1937) 227.

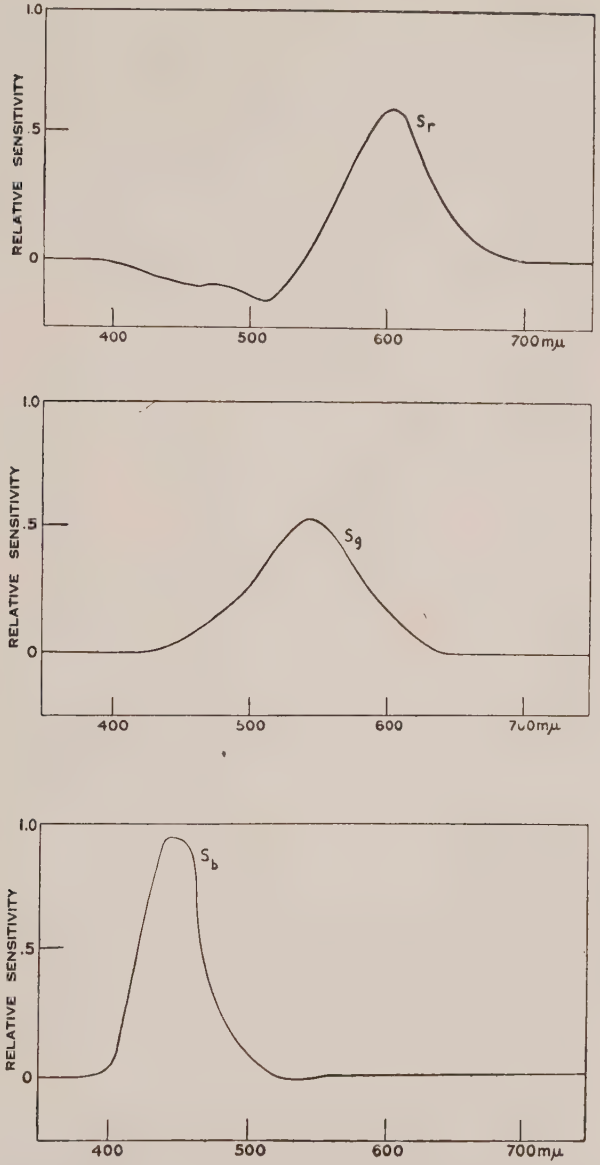

FIG. 389B. Functions S_r, S_g and S_b Represent the Effective Spectral Sensitivities of the Emulsions Used in Making Separation Negatives to Control the Homogeneous Primaries of Figure 389A. (Hardy, *J. Opt. Soc. Am.* 27 (1937), 227.)

S_r, S_g, S_b are the effective spectral sensitivities of the emulsion-filter combinations employed, and x_r, y_r, z_r are dependent on the chromaticity of the synthesis colors. It is evident from these equations that the choice of a given set of additive synthesis colors predetermines the effective spectral sensitivities to be employed when making the color analysis. This fact is clearly evident from calculations by Hardy showing the analysis characteristics required for different synthesis primaries. Fig. 389 shows the effective spectral sensitivity functions required for the widely different synthesis primaries shown in their respective chromaticity diagrams.

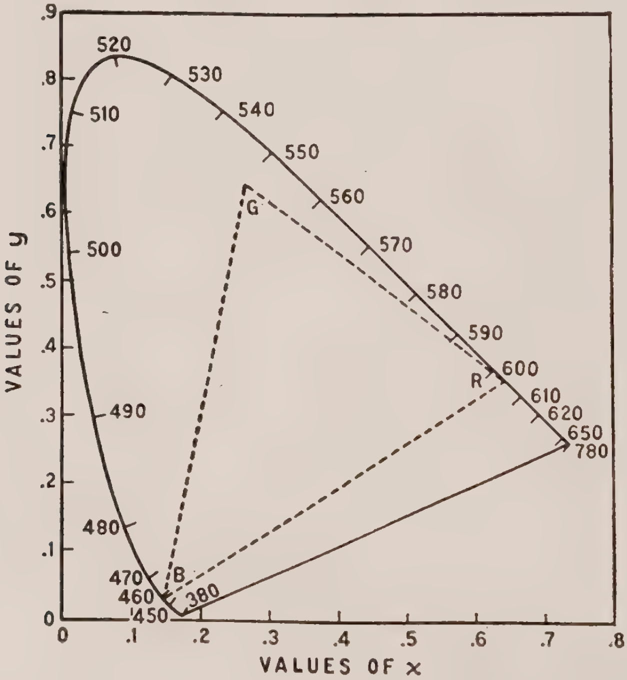

Fig. 389C. Color Gamut Obtainable with Positive Amounts of Nonhomogeneous Primaries. (Hardy, *J. Opt. Soc. Am.* 27 (1937), 227.)

For additive processes, the choice of synthesis colors is based [29] on (1) the widest possible gamut of colors that can be reproduced (taking into account the colors that are apt to be required), (2) the colors that will lead to the smallest practical negative regions for the analysis spec-

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[29] Harrison and Horner, *Phot. J.* 77 (1937) 706. Schaefer and Ackermann, *Z. Physik* 8 (1927) 55.

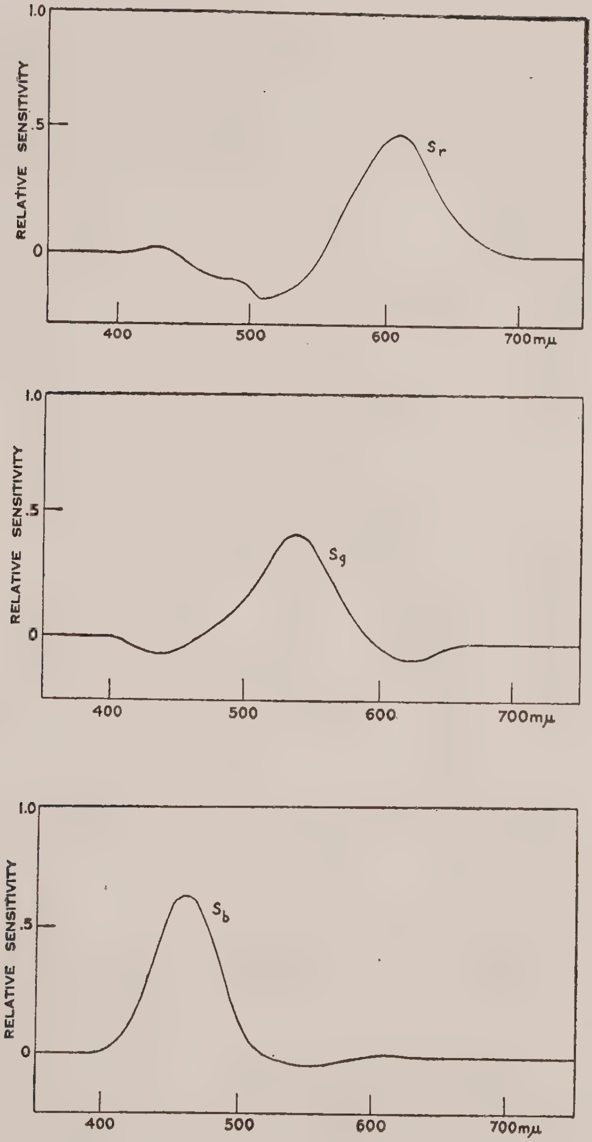

FIG. 389D. Functions S_r, S_g and S_b Represent the Effective Spectral Sensitivities of the Emulsions Used in Making Separation Negatives to Control the Nonhomogeneous Primaries of Figure 389C. (Hardy, *J. Opt. Soc. Am.* 27 (1937), 227.)

tral sensitivities, and (3) the necessity in some cases (non-separable screen plates, for example) of using the same colors for analysis and synthesis. The effective spectral sensitivity curves shown in Fig. 389 are typical of those generally obtained but are not of fundamental importance except for their own special synthesis colors. While the negative regions of such curves vary widely with the synthesis colors employed, the positive portions of the curves are always quite similar. The use of effective spectral sensitivities proportional to the positive portions of the color mixture curves[30] leads to quite accurate reproduction as shown in Fig. 390 (after MacAdam) where the reproductions of the various colors have been displaced towards the center of the chromaticity diagram. A slight increase in the reproduction gamma leads to some

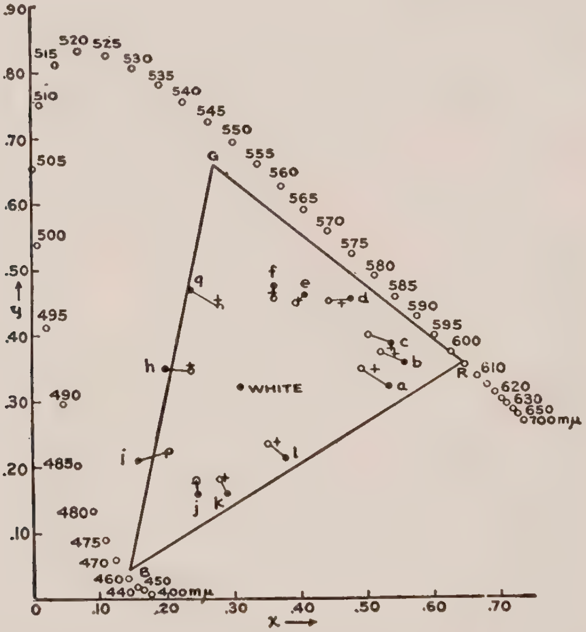

Fig. 390. Calculated Chromaticity Reproductions of: (*a*) Circled Points, an Additive Process Using Spectral Sensitivities Proportional to the Positive Portions of the Color Mixture Curves; (*b*) Crosses, an Additive Process in which Masking is Used to Introduce First Approximations to the Effect of Negative Spectral Sensitivities. (MacAdam, *J. Opt. Soc. Am.* **28** (1938), 399.)

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[30] MacAdam, *J. Opt. Soc. Amer.* **28** (1938) 399.

improvement of the color accuracy,[31] Fig. 391. The negative portions of the spectral sensitivity curves should be taken into account for the most accurate color reproduction. Hardy (loc. cit.) discussed several photographic methods that may be employed, one of them being a form of masking similar to that already discussed, although exposures and not log exposures (densities) should be subtracted by the mask.[32]

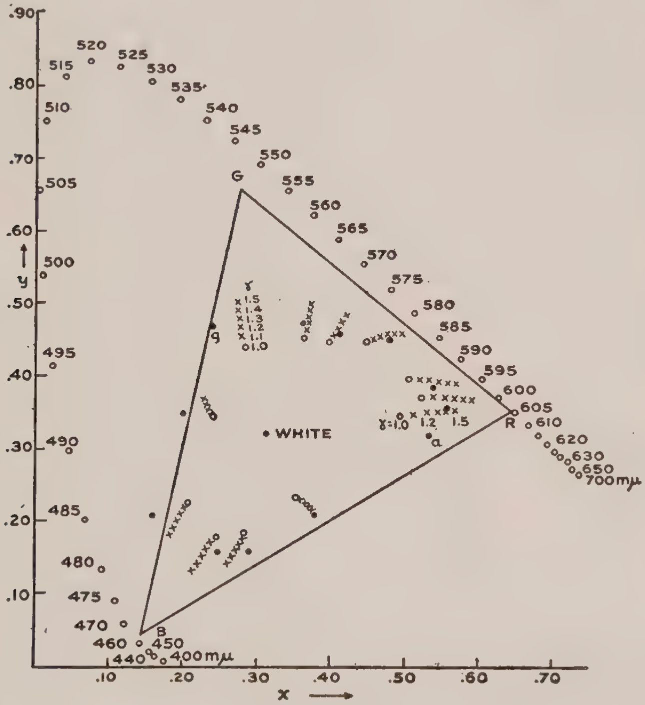

Fig. 391. Calculated Chromaticity Reproductions of Additive Process in which Spectral Sensitivities are Proportional to the Positive Portions of the Spectral Sensitivity Curves. Result of Gamma Changes from 10 to 1.5. (MacAdam, *J. Opt. Soc. Am.* **28** (1938), 399.)

In Fig. 392, for example, the positive and negative portions of the curve may be recorded on separate emulsions and a positive mask from the one recording the negative region registered in contact with the standard negative. The mask will subtract densities. Special toe recording emulsions are necessary to allow exposures rather than densities to be subtracted. Other photographic and electrical means of recording the negative spectral sensitivities have been discussed elsewhere.[33]

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[31] Wright, *Phot. J.* **80** (1940) 25.

[32] Hardy and Wurzburg, *J. Opt. Soc. Amer.* **27** (1937) 227.

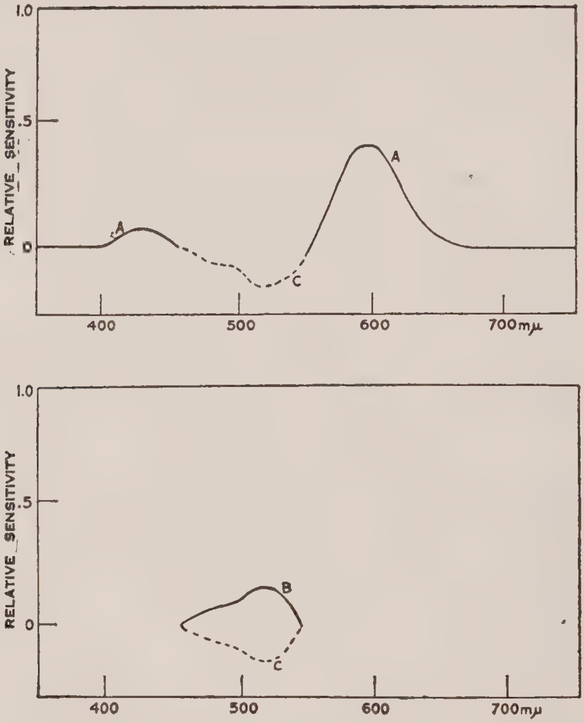
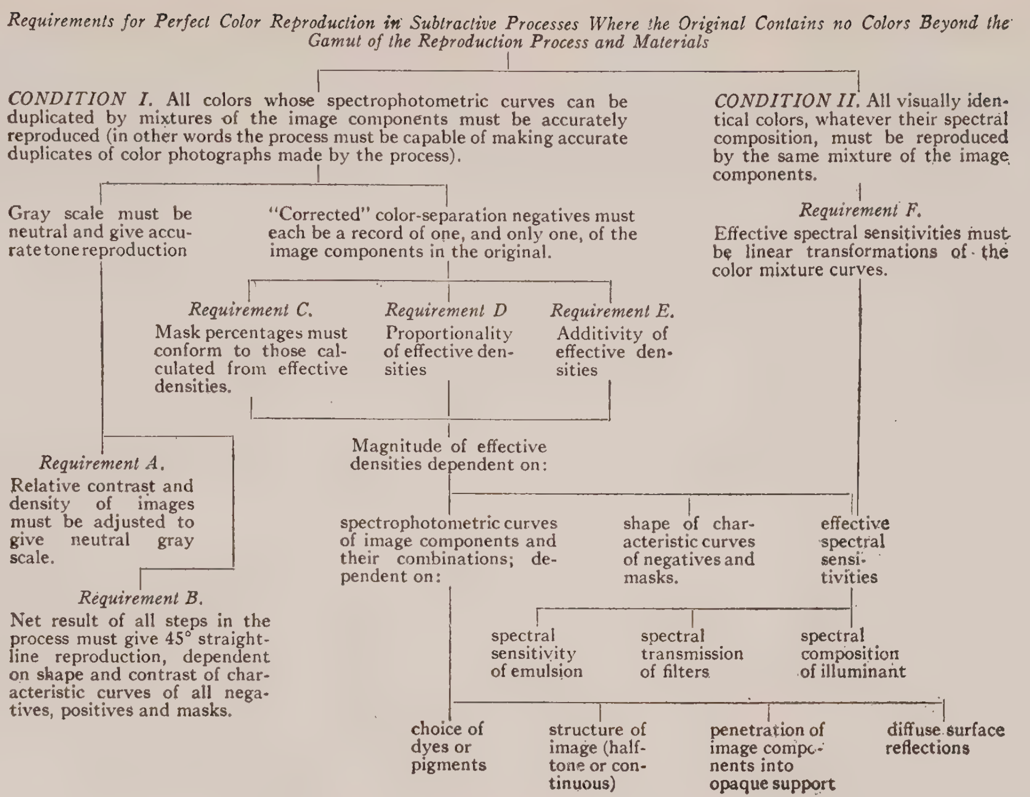


FIG. 392. Combination of Negative and Mask May Yield an Effective Spectral Sensitivity Identical with S_r Function of Figure 389D. (Hardy, *J. Opt. Soc. Am.* 27 (1937), 227.)

Application to Subtractive Color Photography.—An extension of the above theory to subtractive color reproduction is of the greatest importance because of the widespread commercial use of such processes. Subtractive printing colors offer special problems since they do not conform to the simple laws of additive color mixture. With a given cyan dye, for example, two deposits printed one above the other will not necessarily lead to a density equal to the sum of the two original densities and, furthermore, the dominant wave length may shift with the dye concentration. Subtractive printing colors reacting in this manner are called "unstable" because their spectral characteristics are not constant.

[33] *Brit. J. Phot.* **80** (1940) 125, 141, 155.



Requirements for Perfect Color Reproduction in Subtractive Processes Where the Original Contains no Colors Beyond the Gamut of the Reproduction Process and Materials

CONDITION I. All colors whose spectrophotometric curves can be duplicated by mixtures of the image components must be accurately reproduced (in other words the process must be capable of making accurate duplicates of color photographs made by the process).

CONDITION II. All visually identical colors, whatever their spectral composition, must be reproduced by the same mixture of the image components.

Gray scale must be neutral and give accurate tone reproduction

"Corrected" color-separation negatives must each be a record of one, and only one, of the image components in the original.

Requirement F.
Effective spectral sensitivities must be linear transformations of the color mixture curves.

Requirement C.
Mask percentages must conform to those calculated from effective densities.

Requirement D
Proportionality of effective densities

Requirement E.
Additivity of effective densities

Requirement A.
Relative contrast and density of images must be adjusted to give neutral gray scale.

Magnitude of effective densities dependent on:

spectrophotometric curves of image components and their combinations; dependent on:

shape of characteristic curves of negatives and masks.

effective spectral sensitivities

Requirement B.
Net result of all steps in the process must give 45° straight-line reproduction, dependent on shape and contrast of characteristic curves of all negatives, positives and masks.

spectral sensitivity of emulsion

spectral transmission of filters

spectral composition of illuminant

choice of dyes or pigments

structure of image (half-tone or continuous)

penetration of image components into opaque support

diffuse surface reflections

Fig. 393. Yule, *J. Opt. Soc. Am.* **28** (1938), 419.

Since the effective spectral sensitivities to be employed in the color analysis are determined by the printing colors, the indicated sensitivities vary with changes in the printing color conditions and, therefore, cannot be established permanently. MacAdam[34] formulated an approximate law for subtractive color mixtures which made it possible to determine the effective spectral sensitivities necessary for any given set of subtractive colors. In the case of a particular set of acid imbibition dyes the negative regions of the effective spectral sensitivities were insignificant enough to be ignored (see Fig. 394). This is not always the case, however, and appropriate additional masking should be resorted to if the negative sensitivities are any greater than in this particular case.

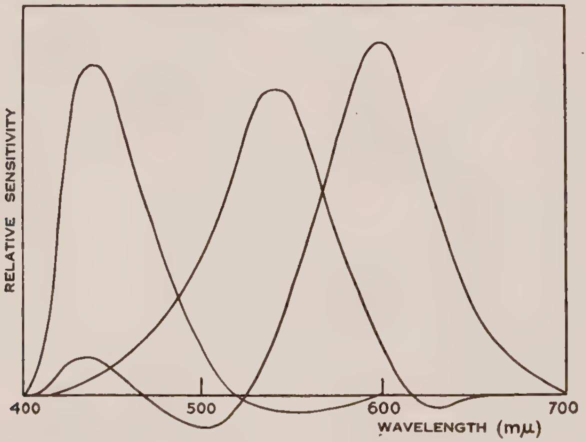


Fig. 394. Relative Spectral Sensitivity Curves. (MacAdam, *J. Opt. Soc. Am.* **28** (1938), 466.)

MacAdam (loc. cit.) and Yule,[35] in an analysis of the factors affecting color reproduction (Fig. 393), showed that masking was essential in subtractive color reproduction to counteract the deficient spectral absorptions of the printing colors. The application of the sensitivities shown in Fig. 394 and the employment of three masks on the separation negatives resulted in excellent color reproduction. The masks for the red and blue separation negatives were obtained from the green separa-

[34] MacAdam, *J. Opt. Soc. Amer.* **28** (1938) 466.

[35] Yule, *J. Opt. Soc. Amer.* **28** (1938) 419, 481.

Miller—J. Opt. Soc. Amer. **31** (1941) 477.

tion negative, while the mask for the green record was obtained from the red separation negative.

It is evident that photographic color correction or masking, discussed earlier in this chapter on the basis of its empirical use, really serves two purposes, both of which are based on sound theoretical considerations. In subtractive color reproduction, masking serves not only as a corrective for the non-ideal spectral characteristics of the printing colors but enables the reproduction to be based on imaginary primaries whose color mixture curves do not have appreciable negative portions.

SUBJECT INDEX

Aberration, chromatic, 76
  spherical, 75
  spherical conditions for the correction of, 93
Aberrations of lenses, 74
  balancing in lens design, 81
Absorption, 56
  of filters, 459
Acetone, in development, 333
Achromatic lenses, 90
Acid dyes, general constitution, 252
Actinometers, 509
Adapters, for film pack, 164
  for roll film, 164
Additive and subtractive reproduction, 736, 817
Adon lens, 118
Adurol, 24, 320
Aerial photography, lenses for, 122
Aero-Tessar lens, 123
Aero-Xenar lens, 123
Agfacolor, 47, 743, 811
Agfa Ultracolor, 788
Air bells, 562
Albumen paper, 25
Alcohol, drying with, 555
Aldis lens, 105
Alkaline development, history of, 25
Alkalis, in development, 332
Amidol, 24, 792
Ammonia, hypersensitizing with, 247
Anastigmat lens, development of, 38
Angle of view, 69
Angulon lens, 96
Antiplanat lens, 37
Aperture, relative, for near objects, 88
  determination of relative, 69
Aplanat, 37, 92
Apo-Planar, 123
Apo-Tessar, 123
Arc lamps, 176, 757
    spectral energy distribution of, 177
  lighting equipment, 181
Aristostigmat lens, 113
Arithmetical coefficient of development, 311
Artar lens, 123
Astigmatism, 77
  conditions for the correction of, 93
Atom, Bohr, 211
  hydrogen, 211
    Sommerfeld's model, 214
  structure of, 211
Atomic structure, 215
Autochrome, 787
Aviar lens, 106
Aviation lens, 123

Backing prints with cloth, 715
Back, reversible and revolving, 147
  repeating, 749
Balmer Series, 209
Bichromated colloids, action of light on, 27, 224, 741, 763, 767
    differential hardening, 779
    insolubilization of by finely divided silver, 741, 763, 768
Biotar lens, 114
Biotessar lens, 111
Bipack, 749, 801
Bis-Telar, 118
Black printers, 822
Bleach-out process, 225, 782
Blocking out the negative, 582
Blue printing, 697
Box camera, 125
Brilliance (color), 456
Bromoil, 28, 682
  bleachers and bleaching, 683
  papers for, 682
  pigmenting, 686
  prints for, 683
  producing the relief, 685

  - transfer, 688
    - operations in transfer, 690
    - transfer papers, 689
    - without a press, 691
- Bromo iodide emulsions, 236

- **Callier** factor, 407
- Calotype process, 14
- Camera, elements of, 124
  - adjustments of, 144
  - first use of, 7
- Cameras, box, 125
  - commercial, 134
  - copying, 139
  - fingerprint, 138
  - hand, 128
  - identification, 139
  - miniature, 130
  - panoramic, 141
  - plate and filmpack, 128
  - pinhole, 124
  - press, 136
  - reflex, 32, 132
  - reproduction processes, 140
  - roll film, 127
  - stereo, 143
  - studio, 135
  - tricolor, 751
  - twin lens, 32, 133
  - view, 134
- Camera obscura, 1
- Carbocyanine dyes, 254, 262
- Carbon process, 27, 662, 768, 774
    - chemical reactions in, 663
    - development, 666
    - double transfer, 667
    - exposing pigment paper, 664
    - final support, 778
    - image transfer, 679
    - increasing sensitiveness, 664
    - on bromide prints, 681
    - sensitizing pigment paper, 663
    - sensitizing, 678
    - single transfer, 665
- Carbro, 28, 676
  - bromides for, 774
  - characteristic curve, 759
  - causes of failure, 682
  - development, 775
  - pigment tissue, 777
  - preparation of celluloids, 776
  - sensitizer, 776
  - temporary support, 778
  - 3 color process, 768, 774
  - transfer, 778
- Catechol, 324
- Celor lens, 99
- Changing bags, 165
- Chloranol, 24, 325
- Chloroquinol, 320
- Chromatic aberration, 76
- Chromaticity diagram, 816
- Chromatone process, 763
- Chrome alum fixing baths, 355
- Chromic acid, 776
- Chromium intensification, 574
- Chromogenic developing agents, 342
- Clark lens, 112
- Clayden effect, 293
- Collinear lens, 96
- Collodion, 764, 782, 789, 803
  - emulsion, 17
  - papers, 26
  - process, 16
- Colloids, for photographic emulsions, 230
  - bichromated, action of light on, 741, 763, 767
  - protective action of, 232
- Collotype, 781
- Color, additive and subtractive, 733, 736
  - additive synthesis, 733, 784, 799
  - attributes of, 456
  - complementary, 740, 816
  - correction, 818, 821
    - distortion, 815, 820
    - effect of light source on reproduction of, 756
    - formation, 762, 805
    - minus, 736, 824
    - subjective, 834
    - trichromatic theory, 733, 815, 835
  - development, 304, 807
    - chemical constitution and dye color, 347
    - chemistry of, 306

    coupler characteristics, 344
    difficulties in, 351
    protected couplers, 812
    substantives, 809
  photography, 44, 733, 833
    additive and subtractive compared, 736, 817
    lenses for, 757
    screen plate process, 738, 784
    subtractive printing processes, 740, 762
    trichromatic theory, 733, 835
    2 color processes, 744
    accuracy, 815, 827
  printing, 740, 818
  reproduction, with photo materials, 456, 815
    accuracy of, 815
  sensitive materials, types, 486, 754, 759
  sensitivity, 437
  sensitizing, early history of, 21
    chart showing development in, 23
  temperature, 168
    effect of voltage on, 172
    measurement of, 169
    of incandescent lamps, 172
    of sunlight, 171
    of various sources, 169
  transparencies, 827
    accuracy of, 827
    reproduction of, 828
Colorimetry, 816
Coloring lantern slides, 726
  photographs, 705
Coma, 78
Combinable lens, 98
Combinar lens, 98
Compensating filter, 790
Compton effect, 218
Contact printing, 616
    exposing print, 616
    printing machines, 617
Cooke triplet lens, 104
Copper reducer, 568
  toning, 656
Corallin, 250
Coupling, dye, 741, 807
Curvature of field, 79
Cut film, 484
Cyanine dyes, history and chemistry of, 252, 254, 257, 260
    classification of, 260
    intermediates for, 264
    linking agents for, 269
    with cycloparaffins linkage, 280
Cyanines, cyano, 289
  five membered, 257
  imino, 289
  preparation of, 272
  simple, 272
  tricyanines, 278
Cyanotype process, 698
Cycloammonium salts, preparation of, 267

Dagor lens, 95
Daguerrotype process, 10
  first in America, 10
  first portrait, 11
Dallon lens, 118
Darkroom, location and arrangement of, 518
  floors, 521
  illumination, 523
  sinks, 522
  ventilation, 521
  wiring, 523
Defects in negatives, 556
Densitometers, 402
  for reflection density measurement, 430
  photoelectric, 404
Density, 56, 401, 406
  exposure relation, 408
  fog, 408
  reflection, 430
Depth of field, 70
    calculation of, 73
  of focus, 71
Desensitization, 791
Developers, ferrous oxalate, 315
  fine-grain, 380
  fogging with, 558
  for lantern slides, 721

  for papers, 599
  for sensitometry, 397
  inorganic, 315
  keeping in solution, 327
  negative, classification of, 533
    contrast, 545
    general purpose, 534
    physical, 547
    rapid, 540
    tropical, 543
    two-bath, 540
  organic, 316
  sodium sulfite in, 330
  tanning, 766
Developing agents, chemical constitution, 317
    chemical identification of, 329
    chromogenic, 342
    coupling, 342
    fogging tendencies, 328
    history of, 24
    rate of exhaustion, 329
    reduction potential, 325
    solubility of, 327
    threshold speeds with, 328
    Watkins' factors of, 551
  papers, 592
    fixation of, 603
    history of, 26
    hypo eliminators for, 604
    sensitometric characteristics of, 436
    stop baths for, 602
    washing of, 604
  solutions, alkalis in, 332
    alkaline bromide in, 334
    effect of dilution on, 339
    effect of use on, 335
    replenishment of, 336
    testing, 337
    the preservative, 330
  tanks, for sheet film, 533
    for roll film, 531
Development, alkaline, history of, 25
  agitation in, 761
  alkalis in, 332
  appearance of over and under, 557
  arithmetical coefficient of, 311
  at high temperature, 543
  by inspection, 550
  calculating for temperatures, 341
  chemistry of with ferrous oxalate, 300
  chemistry of with hydroquinone, 300
  color, 304, 807
  depth, 796
  effect of alkaline bromide, 334
  effect of temperature on, 340
  factor (gamma), 412
  factorial, 551
  factors affecting time of, 549
  horizontal, 548
  hot water, 767, 768, 771, 777
  Knapp's process, 549
  negative control in, 760
  physical, 547
    of lantern slides, 721
  of prints, 592, 599, 601, 602
  P & H process, 549
    in sensitometry, 399
  rapid, 540
  rate of reduction, 310
  reversal, 791, 811, 813
  tank, 760
  temperature effect on, 761
  theory of, 299
  time, 552
  two-bath, 540
  velocity constant of, 314
Diaminophenol, 24, 320
Diazo process, 226, 703, 742
Dicyanine, 257
Diffusing discs, 165
  portrait lenses, 120
Dimethyl-glyoxime, 763
DIN speeds, 420
Diogen, 25
Diorama, 9
Distortion, 80
  color, 815, 820
D log E curve, 408
    effect of development on, 411, 432
    of developing papers, 431, 594
Dogmar lens, 99

Double lens, 35, 91
Drying, 370
    alcohol, 555
    color separations, 755
    infra-red radiation, 554
    rapid, 554
Dry plates, placed on market, 18
        early manufacturers, 20
Dufaycolor, 789
Duplicate negatives, 729
Duratol, 25, 325
Dye bleaching processes, 227
    destruction processes, 227, 742, 801, 805
    coupling development, 304, 308, 807
    processes, photochemistry of, 225
    toning, 658, 660, 764
    transfers, 773
Dyes, acid and basic, 249, 765
    bleeding, 772
    control of color formation, 808
    for imbibition, 772
    intensification with, 581
    mordant for, 764
    retouching with, 590
    sensitizing, 21, 23, 250

Eder-Hecht method, speed determination, 419
Edinol, 324
Eikonogen, 24
Einstein's law, 219
Electro-magnetic waves, lengths of, 50
Elon, 321
Emulsion supports, for negatives, 255, 802
Emulsions, 230
    coating weight, 790
    collodion, 17
    color sensitization of, 250, 754
    gelatin, 18, 231, 234
    integral tripack, 804
    resolving power of, 387
    screen plate, 785
    stripping, 764, 803
    thickness, 786, 804
Ernostar lens, 108
Erythrosin, 250
Etching processes, 779
Ethyl Red, 253
Euryplan lens, 100
Exposure, 503
    appearance of under and over, 557
    color separation negatives, 748
    correction for near objects, 88
    density relation, 408
    factors determining time of, 503
    of prints, 598
    imbibition matrices, 770
    in projection printing, 635
    intensity scale of, 393
    of color screen materials, 790
    range of sensitive material, 429
    time scale of, 393
    to stop motion, 514
    with flash lamps, 200
Exposure meters, 509
    photocell, 511, 513
    visual, 510

Factorial development, 551
Ferricyanide and cyanide reducer, 568
    and thiocyanate reducer, 567
    -hypo reducer, 565
Ferroprussiate, printing process, 697
Ferrous oxalate developer, 300, 315
    sulfate, 24
Field, curvature of, 79
Film, cartridge, 485
    cut, 484
    holders, 163
    pack, 485
        adapters, 164
        cameras, 128
    roll, 485
    sheet, 484
Film base, 477
    cellulose acetate, 479
    cellulose nitrate, 478, 480
    emulsion coating of, 482
    nitrocellulose, introduction by Eastman, 21
    non-deforming, 481
    safety, 481

  special coating, 483
  substratum coating for, 482
Filmcolor, 787
Filter factors, 462
    determination of, 758
    in color photography, 758
Filters, 459
  absorption of, 459
  analysis, 828
  care of, 471
  color, for 3-color photo, 735, 745, 816, 835
    for masks, 823, 824, 828, 832, 833
  compensating, 790
  effect of on spectral sensitivity, 461
  for color selection, 466
  for commercial photography, 469
  for landscape photography, 467
  for orthochromatic reproduction, 466
  for photographing distant objects, 468
  for portrait photography, 469
  optical properties of, 470
  screen plate, 785, 840
  separation, 745
  transmission, 746, 747
  viewing, 467
Finders, 154
Fine-grain developers, 380
Finger print cameras, 138
Finlay process, 792
Fixing, discovery of fixing agent, 6
  baths, acid, 353
    acid hardening, 353
    chrome alum, 355
    effect of use on, 357
    hardening in, 356
    silver thiosulfate compounds in, 352
    testing, 358
  chemistry of, 352
  developing papers, 603
  reaction of hypo with silver halide, 352
  solutions, preparation of, 355
  time required for, 360
Flash lamps, 185
  calculation of exposure with, 200
  characteristics, 187
  determining time-light characteristics of, 188
  effect of battery resistance on firing, 198
  for focal plane shutters, 186
  multiple use of, 197
  reflectors for, 199
  S.M., 199
  spectral distribution of, 189
  synchronization of, 192
  testing synchronization, 198
  time-light curves for, 186
Fluorescent lamps, 175
    lighting equipment for, 182
Focal length, 119
    and size of studio, 120
  plane shutters, 149
Focusing scales, 155
Fog, 558, 758
  density, 408
Fogging tendencies of developing agents, 328
Foot-candle, definition of, 168
Formaldehyde, gelatin hardening with, 355, 771
Fresson process, 674
Front swing, 147
f system, 68

Gamma, 412
  and contrast, 413
  calculation of, 413
  infinity, 416
  reproduction, 447
  time curve, 414
  variation of with wavelength, 464
Gasparcolor, 47, 228, 810
Gauss-type lenses, 112
Gelatin, 231, 804
  hardening in fixing baths, 356
    with alum, 354
    with formaldehyde, 355
  requirements of for photographic purposes, 233
  sensitizing, 233
  soft and hard, 767

Gelatin emulsion, 17, 804
    bromo iodide, 236
    classes of, 234
    early history of, 18
    emulsification, 236
    hardening agents for, 241
    hypersensitizing, 247
    increase in speed by heating, 19
    iodide in, 236
    outline of preparation, 230
    ripening of, 237
    silver halide grain of, 242
    soluble halide in, 239
    stabilizers for, 241
    washing, 239
Gelatino chloride papers, 26
Glass plates, 15, 475, 476
Glue printing, 674
Glycin, 321
Gold toning, 653
Goodwin vs. Eastman, patent infringement, 21
Gotar lens, 123
Gradient, log E curve, 411
    determining minimum, 425
Graininess of image, 375
    factors affecting, 379
    measurement of, 377
Grain size distribution, portrait film and lantern slide, 246
Gray scale, 757
Grotthus-Draper law, 219
Grubb, single lens, 34
Gum bichromate, 28, 669
        coating, 671
        exposure and development, 672
        multiple printing, 673
        preparing paper, 669
    bromide and gum platinum, 674

H & D speeds, 422
Halation, 384
Hand cameras, 128
Hardening solutions, 553
Harrison, gelatin emulsion process, 18
Heliar lens, 106
Heliographic process of Niepce, 7
Herschel effect, 293
High temperature development, 543
Hill, David Octavius, 14
Hill lens, 122
Holders, plate and sheet film, 163
Holostigmat lens, 96
Homocentric lens, 113, 123
Homokol, 254
Horizontal development, 548
Hydramine, 25
Hydrogen atom, 211
        Sommerfeld's model, 214
Hydroquinone, 24, 320
    chemistry of development with, 300
Hydrosulfite toning processes, 654
Hypar lens, 93
Hyperfocal distances, 72
Hypergon lens, 121
Hypersensitizing emulsions, 247
Hypo, discovery of, 6
    chemistry of fixing with, 352
    tests for, 367
Hypo-Alum toning, 645
Hypo eliminators, 369
        for prints, 604

Identification cameras, 139
Illumination, 167
    darkroom, 523
Image, contrast of lens, 85
    granularity of, 375
    spread in emulsions, 382
Imbibition printing, 769
    dye contrast, 773
    dyeing, 772
    dyes for, 772
    expansion of paper, 773
    exposure of imbibition matrices, 770
        masking methods, 825
        wash off relief, 769
Inertia, 422
Infra-red materials, 497
    radiation, drying with, 554
    sensitizers, 259
Inorganic developers, 315

- Integral tripack, historical, 742, 803
  - construction, 803
  - controlled penetration in, 808
  - differential exposure in, 809
  - gelatin emulsion for, 804
  - reversal processing, 811
- Intensification, 573
  - local, 579
  - local with dyes, 581
  - miscellaneous methods, 578
  - of prints, 614
  - sensitometry of, 579
  - with chromium, 574
  - with mercuric-iodide, 577
  - with mercury, 576
  - with silver, 573
- Intensity scale, 393
- Intermittency effect, 391
- Iodide-hypo reducers, 568
- Iron printing processes, 224, 692
  - blueprint, 697
  - Cyanotype, 698
  - kallitype, 701
  - Vandyke, 700
- Isochromatic materials, 22
- Isokol, 254

- **Kallitype** process, 701
- Knapp's process of development, 549
- Kodachrome, 47, 743
  - construction, 743, 803, 813
  - photo-flash lamps for, 191
  - processing, 813
  - types, 743
- Kodacolor, 47, 743
  - color formation, 812
  - construction, 803, 812
- Kodatron lamps, 202
- Kotavachrome, 743, 814
- Kryptocyanine, 256

- **Lamps,** arc, 176, 177
  - flash, 185, 186
  - fluorescent, 175
  - gaseous conductor, 174
  - mercury vapor, 175
  - tungsten, 171
- Landscape photography, filters for, 467
- Lantern slides, 718
  - binding, 728
  - coloring, 726
  - exposure and development of, 718, 721, 723
  - fixing, washing and drying, 721
  - intensification and reduction, 727
  - masking, 727
  - toning, 726
  - varnishing, 727
- Latent photographic image, 290
  - formation of, 295
  - function of sensitivity center, 297
  - Gurney-Mott theory, 298
  - increase in with time, 290
  - metallic silver theory, 294
  - physical theories, 294
  - quanta required to produce, 222
  - reactions of, 292
  - stability of, 290
  - sub-halide theory, 294
  - theories of, 293
- Lens, aberrations of, 74
  - adapter, 164
  - first use of, 2
  - → formulary, 86
  - magnification produced by thin, 61
  - mount, swinging, 166
  - principal points of, 64
  - shades, 163
  - shapes of positive and negative, 61
  - thin in air, 60, 64
- Lenses, achromatic, 90
  - based upon Petzval Portrait lens, 102
  - contrast of image, 85
  - double, 35, 91
  - entrance and exit pupils of, 67
  - five lens cemented type, 98
  - focal length and size of studio, 120
  - for aerial photography, 122
  - for photographing whole sky, 121
  - for portrait work, 119, 120
  - for reproduction processes, 123
  - four cemented lens type, 97
  - Gauss type, 112

- history of photographic, 34
- loss of light in, 84
- resolving power, 82
- single, 34, 90
- soft focus, 92
- surface coating of, 85
- telephoto, 41, 117
- triplet, 93, 104
- triplet with rear doublet, 108, 110
- wide angle, 121

Lenticular process, 798
Light, 48
- absorption of, 56
- and illumination, 167
- intensity, 167
- polarized, 55
- reflection and refraction, 53
- reflection of by a spherical surface, 57
- sources of, 167, 756
- wave front, 54
- wave motion, 49

Light sensitive materials, for photography, 221
Light diffusing materials, 184
Light filters, 459
Light reflecting surfaces, efficiency of, 184
- refraction of at spherical surface, 59

Light sources, effect on spectral sensitivity, 458
- for sensitometry, 393
- spectral energy of, 168

Lighting equipment, 177
- Arc, 181
- care of, 182
- for commercial and illustrative photography, 179
- for fluorescent lamps, 182
- for portrait photography, 178
- for Tungsten lamps, 177
- in color photography, 756
- portable, 180

Linear lens, 98
Lippman process, 44
Local reduction, 579
Lumen, 167
- second, 187

Luppo-Cramer effect, 293

Magazines, for plates and sheet film, 165
Magia Naturalis, 1
Marten's densitometer, 403
Masking, 821, 825
Masks, positive, 822
- silver, 832
- single, 833

Mercury, hypersensitizing with, 247
- intensification with, 576, 577

Mercury-sulfide toning, 656
Mercury vapor lamps, 175
Meritol, 325
Merocyanines, 280
- classification of, 281
- intermediates for, 282
- linking agents for, 283
- preparation of, 283
- sensitizing properties of, 285

Metallic silver theory of latent image, 294
- toning, 762

Metol, 24, 321
Metoquinone, 24, 325
Metrogon lens, 113
Miniature cameras, 33, 130
Minicolor, 743, 814
Minimum gradient speed, 423, 425
Monomet, 25, 325
Mordants, 659, 764, 765
Mosaic screen, 786
Mounting prints, 708
- commercial mounts, 713
- double, 713
- dry, 714
- on cloth, 715
- preparing embossed, 712
- preparing line mount, 711
- preparing slip-in-mount, 711
- with paste, 714

Naphthenone, 251
Negative, blocking out, 582
- intensification of, 573

- introducing black backgrounds, 583
- retouching portrait, 584
- stripping, 589
- titling, 583
- varnishing, 588

Negative developers, 533
  - classification of, 534
  - contrast, 545
  - fine grain, 534
  - general purpose, 534
  - physical, 547
  - rapid, 540
  - tropical, 543
  - two-bath, 540

Negative development, factorial, 551
  - fine-grain, 534
  - horizontal, 548
  - inspection, 550
  - physical, 547
  - rapid, 540
  - two-bath, 540

Negative masks, 832

Negative materials, choice of, 489
  - color sensitive, 22, 486
  - latitude of, 428
  - resolving power of, 389
  - spectral response of, 457

Negative processes, on glass, 15

Negatives, defects in, 556
  - enlarged, 731
  - making duplicate, 729
  - paper, 486, 731
  - reduction of, 565
  - removing gelatin backing of, 590
  - three-color, 745, 748, 754, 760, 796

Neocyanine, 257

Neol, 25, 325

Newton's rings, eliminating, 633

Nitrocellulose film, introduction by Eastman, 21

Non-halation materials, 385

Objectives, achromatic, 90
  - for aerial photography, 122
  - apanat, 92
  - development of anastigmat, 38
  - double, 35, 91
  - five-lens cemented type, 98
  - for portrait work, 119
  - for reproduction processes, 123
  - four-lens cemented type, 97
  - Gauss type, 112
  - history of photographic, 34
  - Petzval Portrait lens, 102
  - single, 90
  - soft focus, 92
  - telephoto, 41, 117
  - three-lens cemented type, 94
  - triplet, 93, 104
  - triplet lenses with rear doublet, 108, 110
  - wide angle, 121

Omnar lens, 113

One-shot camera, 751

Opacity, 56, 401

Opic lens, 114

Optical glass, index of refraction typical, 54

Organic developers, 316

Orthochromatic filters, 466

Orthochromatic materials, 22, 487

Orthochromatic reproduction, 464, 466

Orthochrome T, 253

Orthometar lens, 100

Orthoscope lens, 41

Orthostigmat lens, 96, 123

Ortol, 24, 324

Ozobrome, 28

Ozotype, 28

P & H process, 549

Palladium printing, 695

Panchromatic materials, placed on market in England, 22
  - wedge spectrograms of, 489
  - negative materials, 487

Panoramic cameras, 141

Pantachrome, 799

Pantar lens, 98

Paper negatives, 731

Paraminophenol, 321

Paraphenylene diamine, 24

Parikol, 254

Pellicle, 754

Pentacarbocyanines, 259, 279

Pentac lens, 111
Periodicals, photographic, 47
Permanganate reducers, 569
Persulfate reducers, 571
Petzval orthoscope lens, 41
    portrait lens, 34, 102
Photocell exposure meters, 511, 513
Photochemistry, 3, 206
    bichromate processes, 224
    dye processes, 225
    Einstein's law, 219
    iron processes, 224
    laws of, 219
    nature of reactions, 220
    quantum energy of different radiations, 207
    silver processes, 221
Photochromoscope, 737
Photoelectric effect, 207
        quantum yields, 228
Photoflash lamps, characteristics of, 190
    for Kodachrome, 191
    time-light curves for, 186
Photogenic drawing, 14
Photographic image, optical characteristics of, 406
        graininess of, 375
        sharpness of, 381
Photography, definition, 1
Photometric constant, 401
Photon, 207
    collisions between, 217
    energies, 208
Photostat, 143
Physical development, 547
Pigment processes, 27, 662
        bromoil, 682
        carbon, 662
        carbro, 676, 677
        gum, 669
        miscellaneous, 674
        powder, 675
Pigments, 3-color, 777, 819
Pinachrome, 254
Pinacyanol, 256
Pinaflavols, 285
Pinatype, 780
Pinaverdol, 254
Pinhole camera, 124
Planar lens, 112
Planck's Constant, 207
Plasmat lens, 100
Plastigmat lens, 92
Platinotype process, 692
        Clerc's process, 694
Polarizing screens, 472
Polymethines, 259, 263
Polysulfide toning, 648
Portrait cameras, 135
Portrait photography, lenses for, 119
Powder printing processes, 675
Press camera, 136
Primary colors, 733
Printing colors, 740, 818
Printing, contact, 616
    projection, 620
Printing machines, 617
        difficulties with, 620
        photofinishing, 619
        professional, 618
Printing papers, albumen, 25
        bichromated history of, 27
        bromoil, 28, 682
        carbon, 27, 662, 768, 774
        carbro, 28, 676, 677, 774
        choice of surface and color, 596
        collodion, 26
        cyanotype, 698
        developing, 26, 592
        D log E curve of different emulsions, 594
        Diazo, 226, 703
        Ferroprussiate, 697
        gelatino chloride, 26
        gum pigment, 669
        Kallitype, 701
        miscellaneous pigment, 674
        oil, 28
        Ozotype, 28
        palladium, 695
        platinum, 27, 692
        powder, 28, 675
        sensitometry of, 430

    subtractive for color photography, 740, 763
    surface and colors of, 593
    tone reproduction on, 454
    Vandyke, 700
    variable contrast, 595
    wash-off relief, 769
    with iron salts, 692
    with silver salts, development of, 25
Prints, coloring, 705
  making vignetted, 613
  mounting, 708
  permanence of, 615
  reduction and intensification of, 614
  for reproduction, 611
  rush, 610
  spotting, 716
  tinting, 705
  trimming, 706
  varnishing, 717
  washing of, 604
  waterproofing, 717
  waxing, 716
Processing latitude, 416
Projection printing, 620
    control in, 638, 639, 640
    correction of distortion, 641
    determining exposures, 635
    equipment, 629
    light sources, 621
    negative illumination, 622, 624
    negatives for, 632
    from wet negatives, 641
Proportional reducers, 570
Protar lens, 97
Pyrocatechin, 24, 324
Pyrogallol, 24, 323

Quanta, 206
  required for latent image formation, 221
Quantum energy of different radiations, 207
  mechanics, 216
Quantum, numbers, 213
Quantum Theory, restrictions of, 216
Quantum yields of photographic reactions, 228

Radiar lens, 110
Radiation, 48
  discontinuous, 51
  quantum theory, 206
Raman effect, 218
Range finders, 156
    split-field type, 159
    superimposed image type, 159
Rapid rectilinear lens, 37, 92
Reciprocity effect, 390
Rectigraph lens, 143
Reducers, 565
  Belitzski, 569
  copper, 568
  ferricyanide-cyanide, 568
  ferricyanide-hypo, 565
  ferricyanide and thiocyanate, 567
  iodide-hypo, 568
  iodine-cyanide, 568
  permanganate, 569
  persulfate, 571
  superproportional, 570
Reduction, 565
  local, 579
  of prints, 614
  proportional, 570
  subtractive, 565
Reduction potential, of developing agents, 326
Reflection characteristics of printing colors, 818
Reflex camera, 32, 132
Refraction, index of, 53
    at spherical surface, 59
Relative aperture, 68
    determination of, 69
    for near objects, 88
Relief imbibition printing, 769
  processes, 765
Repeating back, 749
Reproduction process cameras, 140
  lenses for, 123
Resinopigmentype process, 674

Resolving power, lenses, 82
    of photographic materials, 386, 389
Retouching portrait negatives, 584
  the face, 586
  individual features, 587
  modeling, 586
  with dyes, 590
Roller-blind shutters, 43
Roll film, 485
    adapters for, 164
    cameras, 127
    developing tanks for, 531
Rubinol, 323
Rydberg Constant, 210

Safety base film, 481
Scheiner speeds, 418
Schwarzschild constant, 391
Scratch proofing solutions, 553
Screen plates, early, 46
    autochrome, 787
    Dufaycolor, 789
    copying, 793
    duplication of, 793
    emulsions, 785
    exposure, 790
    filmcolor, 787
    filters, 785, 840
    Finley, 792
    geometric, 787
    inseparable, 787
    mosaic, 787
    negative-positive processing, 795
    principles of, 738, 784
    processing, 791, 795
    requirements, 785
    separable, 792
    3-color negatives from, 796
    ultracolor, 788
Selenium toning processes, 655
Self-timers, 165
Sensitivity centers, function of in exposure, 297
Sensitivity, of silver halide grain, 243
  spectral, 437
Sensitizing dyes, acid, 250
    basic, 252
    carbocyanine, 254, 262, 275, 279
    cyanine dyes, 252, 257, 260, 261, 289
    erythrosin, 21, 250
    history of, 21, 23
    infra-red, 259
    merocyanines, 280
    naphthenone, 251
    pentacarbocyanines, 259
    polymethine dyes, 259
    selenacyanines, 258
    tetracarbocyanines, 259
    thiaxanthone, 251
    tricarbocyanines, 259
    triphenylmethanes, 250
Sensitizing gelatin, 233
Sensitol Green, 254
Sensitometers, 393, 394, 395, 396
  Eastman 2B, 396
  monochromatic, 437
  optical wedge type, 393
  time scale instruments, 395
  tube, 394
Sensitometry, 390
  color sensitometry, 436
  densitometers, 402
  developers and development, 397, 399
  D log E curve, 408
  of intensification, 579
  light sources, 392
  of printing papers, 430
Sharpness of image, 381
    variation with emulsion, 383
    variation with wavelength, 383
Sheet film, 484
  developing tanks for, 533
  magazines for, 165
Shutters, 42, 148
  before the lens, 148
  behind the lens, 148
  between the lens, 149
  efficiency of, 152
  focal plane, 149
  roller-blind, 43

- rotary, 43
- speed of, 151

Sigmar lens, 93
Silver, intensification with, 573
Silver chloride, studies on the decomposition of, 3, 4
Silver dye bleach process, 227
Silver grain, structure of, 374
Silver halide, reaction of hypo with, 352
- size frequency curves, 246
- structure of molecule, 296

Silver halide grain, 242
- development of, 373
- distribution of in emulsion, 244
- sensitivity of, 243

Silver processes, photochemistry of, 221
Silver recovery, 361
- electrolytic methods, 364
- sodium sulfide, 362
- with zinc, 363

Single lenses, 90
Sliding back, 749
Sodium hydrosulfite developer, 316
Sodium sulfite, in developers, 330
Sonnar lens, 108
Spectra, 209
- Balmer Series, 209
- band, 217
- x-ray, 210

Spectral energy, 168
- Arc lamps, 177
- Flash lamps, 189
- Fluorescent lamps, 175
- incandescent tungsten, 168
- Mercury vapor lamps, 175

Spectral sensitivity of negative materials, 457
- effect of filter on, 461
- effect of light source, 458

Spectograms, interpreting, 438
Spectrophotometer, 816
Spectrum, electro-magnetic, 50, 208
Speed determination, comparison of various systems, 508
- Chapman Jones, 419
- DIN method, 420
- Eder-Hecht method, 419
- H & D method, 422
- minimum gradient method, 422
- Scheiner method, 418
- threshold methods, 418
- Warnerke's method, 419
- Weston method, 422

Spherical aberration, 75
- correction of, 93

Stains on negatives, 559
- aluminum sulfite, 562
- developer, 559
- green, 562
- removing, 560
- silver, 561
- sulfur, 561
- yellow, 560

Stannous salts, toning with, 654
Stefan's law, 51
Stereo cameras, 143
Stereo attachment, 166
Stripping emulsions, 764, 803
Stripping negatives, 589
Structure of image, 373
Sub-halide theory of latent image, 294
Subjective color, 834
Substratum coating, 482
Subtractive synthesis, 736
- color correction in, 818

Subtractive printing processes, Table, 45, 763
Sulfur toning processes, prints for, 644
- acid hypo, 648
- direct sulfide processes, 649
- indirect processes, 650
- with Polysulfides, 648

Sunlight, variation in intensity of, 170
- variation and color temperature of, 171

Superproportional reduction, 570
Sury's printing process, 675
Swingback, 144, 145
Swingfront, 147
Synchrograph, 187
Synchronizers, 194, 196
- testing accuracy of, 198

Syntor lens, 99

Technicolor, 767
Telegor lens, 118
Teleobjectives, 41, 117
Teleros lens, 118
Tele-Tessar lens, 118
Telic lens, 118
Tessar lens, 108
Tetracarbocyanines, 259
Thiaxanthone, 251
Thin lenses, systems of, 64
Three-color negatives, 745
    development, 759
    exposing, 748, 758
    filter factors, 758
    lenses for, 757
    reference object, 757
    from screen plates, 796
    sensitive materials for, 754
Three-color sensations, 734, 833
Time-gamma curve, 414
Time scale, of exposure, 393
Tinting photographs, 705
Titling negatives, 583
Tone reproduction, 440
    analysis of, 450
    gamma product, 447
    graphical solution of, 448
    of neutral gray object, 442
    orthochromatic, 464
    on printing papers, 454
Toning, silver images, 763
  copper, 656
  direct sulfide, 649
  dye, 658, 764
  gold, 653
  hydrosulfite, 654
  hypo-alum, 645
  mercury-sulfide, 656
  metallic, 762
  polysulfides, 648
  selenium, 655
  sulphur processes, 644
  tin, 654
  uranium, 656
  vanadium, 658
  with acid hypo, 648
Toning lantern slides, 726
Transparencies, 728
Transparency, 56, 401
Tricarbocyanine dyes, 259, 278
Trichromatic theory, 733, 833
Tricolor cameras, types, 751
Tripacks, 45, 742, 749, 801, 803
    construction, 803
  controlled penetration in, 808
  emulsion characteristics of, 804
Triphenylmethane dyes, 250
Triplet lenses, 93, 104
Tripods, 162
Tristimulus values, 816
Tropical developers, 543
Tungsten light sources, 171
    color temperature of, 172
    lighting equipment for, 177
    spectral energy curves of, 168
Turner-Reich lens, 98
Twin lens camera, 133
Two-bath developers, 540
Two-color processes, 444

Ultracolor screen plates, 788
Unar lens, 108
Unofocal lens, 117
Uranium toning process, 657
Utocolor, 782

Vanadium toning, 658
Vandyke process, 700
Varnishing lantern slides, 727
  negatives, 588
  prints, 717
Velocity constant of development, 314
Velostigmat, 101
Velox, 26
Verito lens, 92
View cameras, 134
Vignetted prints, 613
Villard effect, 293
Vitachrome, 782
Voltage regulating devices, 173
Voltage, variation in color temperature with, 172

Washing, time of, 364
  papers, 604
  tests for, 367

Wash-off Relief process, 771
  dyeing, 772
  paper preparation, 773
  transferring color images, 773
Watkins' factor, 551
Wavelengths, units of measurement, 206
Waxing prints, 716
Wedge spectograms, 438
Weston speeds, 422
Wide angle lenses, 121
Wide Angle X-Press lens, 100
Wien's law, 51

X-ray spectra, 210

INDEX OF AUTHORS

Abegg, 243, 301
Abney, 24, 236, 391
Adams and Haller, 256
Albert, 293
Aldis, 105
Andresen, 24, 317, 330, 331, 779
Arago, 9, 294
Aristotle, 1

Bacon, Roger, 1
Baekeland, 26
Balmer, 209
Bancroft, 301
Barbaro, Daniello, 2
Barkla, 210
Bausch and Lomb Co., 112, 113, 121, 123
Bayer, 254
Becquerel, 43
Belicke, 108
Belitzski, 569
Bennett, 19
Bertele, 106
Berthollet, 294
Berthon, 797
Bohr, 211
Booth, 111, 118
Bowen, 224
Bragg, 210
Brooker, 281
Bull, 746, 835
Bunsen and Kirchoff, 208
Burgess, 18

Callier, 393, 407
Capstaff, 536
Carrol, 236
Champlin, 539
Charles, 583
Chevalier, 8, 34
Christensen, 805
Clarke, 330
Clerk-Maxwell, 44, 48, 733, 833
Conklin, 377
Crabtree, 378
Crabtree, Eaton and Muehler, 369, 604
Crabtree and Henn, 536
Crabtree and Muehler, 574
Cros, 780

Daguerre, Louis Jacques, 8
Dallmeyer, 37, 91, 102, 111, 113, 117, 118
Davisson and Germer, 217
de Broglie, 216
Dersch and Duir, 247
du Hauron, Louis, 44, 46, 742, 784, 803
Dunham, 377

Eastman, George, 20, 26, 35
Eder, 19, 21, 224, 236, 243, 663
Eder and Pizzighelli, 26
Eder and Toch, 24
Edwards, 780
Eggert, 228
Eggert and Noddack, 221, 223, 291
Einstein, 207
English, 247
Ermen, 329, 330
Evans and Hanson, 302, 331

Farmer, H., 768
Ferguson, 552
Finlay, 792
Fischer, 255, 256, 304, 305, 807
Frederick & Altman, 103
Freer, 227

Glover, 724
Goerz, C. P., 95, 96, 98, 99, 118, 121
Goetz, 378
Goldberg, 393
Goodwin, Hannibal, 21
Green, Cross and Bevan, 227
Greiss, 227
Grotthus, 219

Grotthus-Draper, 782
Grubb, 90
Gurney and Mott, 298

Haddon and Banks, 244
Hamer, 257, 259, 262, 270
Hardy, 835
Harting, 106
Hasselkus, 98, 110
Heisenberg and Born, 217
Herschel, Sir John, 1, 6, 15, 27
Hickman and Spencer, 604
Hill, Robert, 122
Hodgson, 300
Hofmann, 257
Homolka, 22, 304, 807
Hubl, 328
Hughes and Atkinson, 330
Hughes and Mullendyke, 237
Hugo Meyer, 100, 113, 115
Hurter and Driffield, 401, 552
Hymer, 227

James, 222, 303
Joly, 784
Jones, 435, 454
Jones and Deisch, 377
Jones and Hardy, 377
Jones and Morrison, 436

Kampfer, 97
Kaufmann and Vonderwahl, 254, 255
Kendall, 259, 281
Koch, 222
Koegel and Neuenhaus, 704
Kogel, 226, 227
Kollmorgen, 113
König, 22, 253, 254, 256, 258, 259

Lasreff, 226
Lee, 103, 106, 114, 118, 119
Le Gray, 15, 25
Lehrmann and Busch, 358
Lehrmann and Tausch, 330, 331
Liesegang, 225, 779
Limmer, 225
Lippman, 43
Lowry, 377
Lumiere, 24, 25, 325, 787
Lumiere and Seyewetz, 224, 317, 322, 369, 536, 663
Lüppo-Cramer, 244

MacAdam, 840, 844
McFarlane, 393
McQuown, 547
Maddox, Richard Leach, 18
Manly, 28
Mansfield, 19
Marion, 28
Martin, 113, 117
Mees, 244, 377
Mees and Piper, 329
Mees and Wratten, 548
Merte, 98, 114
Miethe, 22
Miethe and Traub, 253
Milbauer, 328
Millikan, 208
Mills, 253, 255, 257
Mills and Adams, 257
Mills and Braunholtz, 256
Mills and Hamer, 256
Mills and Koch, 254
Monkhoven, 19, 236
Mosely, 211
Mott, 224
Mudrovcic, 226
Murray, 302

Namias, 674
Nelson, 426
Newton, 208
Niepce, Isidore, 9
Niepce, Joseph Nicephore, 6
Niepce, de Saint Victor, 15
Nietz and Huse, 579
Norris, 17

Odell, 547
Ostwald, 301

Pauli, 215
Penney, 236
Piggott, 270
Pinnow, 331

Planck, 51, 206
Plauman, 330
Poitevin, 27
Ponton, 27
Porta, Jean Baptiste, 1

Rabinovitch, 302
Reinders, 302
Renwick, 244, 294
Renwick and Sease, 237
Ross, Andrew, 34
Ross Ltd., 98, 100, 110, 113, 118
Ross, Thomas, 37
Rudolph, 39, 95, 96, 97, 100, 108, 112, 115
Rutherford, 211
Rydberg, 209

Sayce and Bolton, 17
Schade, 104
Scheberstow, 329
Scheele, Carl Wilhem, 4, 293
Schinzel, 803
Schneider, 96, 111, 123
Schrodinger, 217
Schulze, Johann Heinrich, 3
Schwartz, 302
Schwarzschild, 391
Scott-Archer, Frederick, 16
Sease, 539
Seebeck, 43
Sheppard, 233, 235, 300, 301, 592, 650
Sheppard and Mayer, 301
Sheppard and Mees, 300
Sheppard and Trivelli, 236
Sheppard, Wightman and Trivelli, 245
Slade and Higson, 244
Smethurst, 247
Smith, 782
Sommerfeld, 214
Southall, 815
Spalteholtz, Hoogewerff and Van Dorp, 253
Spencer, 835
Staude, 303
Steinheil, 36, 37, 93, 96, 117
Stenger, 1
Strauss, 329
Svedberg, 245, 300
Swan, 27

Talbot, 13
Taylor, H. D., 40, 104, 105
Taylor, Taylor and Hobson Ltd., 101, 102, 103, 104, 106, 114, 118, 119
Thomson, 701
Tritton, 664
Trivelli, 237
Tronnier, 96, 111
Tull, 307
Tuttle, 598, 626

van Kreveld, 835
Venn, 684
Vogel, 21, 253
Voightlander, 30, 96, 97, 102, 106
Volmer, 301
Von Hoegh, 95, 98, 99, 121

Wahl, 270
Walter, 258
Warmisham, 102, 103, 106
Waterhouse, 21
Watkins, 551, 552
Webb, 222, 223, 224, 835
Webb and Evans, 223
Wedgwood, Thomas, 4
Wendt, 226
Weyde, 369
Wightman, Trivelli and Sheppard, 224
Williams, 252
Willis, 27
Wilsey, 237
Wright, 73, 815
Wunsch, 733

Young, Thomas, 48, 733, 833
Yule, 843, 844

Zeeman, 214
Zeiss, 96, 97, 98, 100, 108, 110, 111, 112, 114, 121, 122
Zschokke, 96